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### StormFilter material testing summary report – Localized performance of bio- and mineral-based filtration material components

Wendling, Laura; Loimula, Kalle; Kuosa, Hannele; Korkealaakso, Juhani; Iitti, Hanna; Holt, Erika

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VTT  
<http://www.vtt.fi>  
P.O. box 1000FI-02044 VTT  
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# StormFilter Material Testing Summary Report

## Localized performance of bio- and mineral-based filtration material components

Authors: Laura Wendling, Kalle Loimula, Hannele Kuosa, Juhani Korkealaakso, Hanna Iitti and Erika Holt

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<b>Summary</b> <p>Effective urban stormwater runoff purification and management is vital for freshwater resource protection and the potential use of stormwater to augment urban water supply. Pollutant discharge from roads, ports and cities in urban stormwater runoff is an unintended consequence of human habitation and use of ecosystem services, which can be mitigated to reduce pressures on local water resources. Conventional wastewater treatment systems are largely unsuitable for stormwater treatment as only water entering sewer networks can be treated in municipal facilities. Engineered structures for passive water treatment are widely recognized as a cost-effective means of attenuating diffuse pollution. The capacity of selected geo- and bio-based filter material to remove the common stormwater contaminants phosphorus, copper, lead, zinc, chloride and sulfate from water was determined in batch tests using a synthetic solution representative of a 'first flush' of stormwater following a prolonged dry period. The ability of each solid material to remove selected common stormwater contaminants from flowing water was subsequently determined in column experiments using the same synthetic stormwater solution. Additional column trials were conducted using individual filter materials and ten-fold concentrated influent synthetic stormwater. Results of the present research provide an improved understanding of the behavior and fate of selected nutrient and metal contaminants within engineered infiltration systems for urban stormwater treatment, facilitating effective long-term management of urban water resources.</p>	
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<b>VTT's contact address</b> VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, FI-02044 VTT, Finland	
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## Executive Summary

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Effective urban stormwater runoff purification and management is vital for freshwater resource protection and the potential use of stormwater to augment urban water supply. Extensive changes in land use have substantially increased pollutant loads to aquatic environments in many regions. Pollutant discharge from roads, ports and cities in urban stormwater runoff is an unintended consequence of human habitation and use of ecosystem services, which can be mitigated to reduce pressures on local water resources. Conventional wastewater treatment systems are largely unsuitable for stormwater treatment as only water entering sewer networks can be treated in municipal facilities. Engineered structures for passive water treatment are widely recognized as a cost-effective means of attenuating diffuse pollution. Results of the present research provide an improved understanding of the behavior and fate of selected nutrient and metal contaminants within engineered infiltration systems for urban stormwater treatment, facilitating effective long-term management of urban water resources.

The capacity of selected geo- and bio-based filter material to remove the common stormwater contaminants phosphorus, copper, lead, zinc, chloride and sulfate from water was determined in batch tests using a synthetic solution representative of a 'first flush' of stormwater following a prolonged dry period. These results showed:

- All of the solid materials tested demonstrated some ability to remove copper, lead and zinc from synthetic stormwater, except the crushed rock aggregate which had limited capacity for lead removal.
- Nearly all of the solid materials tested successfully removed phosphorus from solution, except the crushed rock aggregate and the birch biochar. The crushed rock aggregate removed only a very small quantity of phosphorus from solution, which was too little to be of practical significance in stormwater treatment. The birch biochar released phosphorus from the solid phase into solution, resulting in a net increase in solution phosphorus concentration.
- None of the solid materials tested showed substantial capacity for sulfate or chloride removal.

The ability of each solid material to remove selected common stormwater contaminants from flowing water was determined in column experiments using the same synthetic stormwater solution representative of a 'first flush' of stormwater following a prolonged dry period. Additional column trials were conducted using individual filter materials and ten-fold concentrated influent synthetic stormwater. Column trials using single materials within columns showed:

- None of the materials tested demonstrated substantial sulfate or chloride retention.
- All materials examined effectively removed copper, lead and zinc from both the 'normal' first-flush stormwater and the ten-fold concentrated stormwater.
- The sorption capacities of filter materials were not reached in either of the column trials using 'normal' or ten-fold synthetic stormwater concentrations.
- With the exception of the birch biochar, all materials demonstrated effective removal of phosphorus. Consistent with the results of batch testing the birch biochar showed a net release of phosphorus when influent solution phosphorus concentration was low, observed as a small net increase in phosphorus concentration in effluent relative to influent water. Phosphorus was retained by the birch biochar at greater influent phosphorus concentrations, indicating a strongly concentration-dependent mechanism of phosphorus retention by the birch biochar filter material.

Additional column trials and up-scaling experiments are underway using different combinations of filter materials in various layer configurations. The pH of influent synthetic stormwater will be controlled in further experiments to minimize flocculation and/or precipitation of metals and phosphorus in solution during the experiment. Geochemical modelling will be used to elucidate potential chemical mechanisms of pollutant attenuation in layered filter systems.

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Authors

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## 1. Introduction

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Urban stormwater runoff can negatively impact surface waters and groundwaters in and near urban areas. Cloudbursts and the resultant rapid stormwater runoff and network overflows are increasingly common in urban areas due to widespread impervious surfaces, changing precipitation patterns as a consequence of climate change, aging infrastructure, and often undersized, centralized stormwater networks. Estimates suggest that Finland will be subject to a 20% increase in stormwater volume by the year 2050<sup>1</sup>. In addition to increases in stormwater volume, urban water collection systems are also burdened by increasing urban populations. According to the Population Reference Bureau, by the year 2050, 84% of the world's population will be living in urban and suburban areas<sup>2</sup>. Cities must simultaneously ensure compliance with legislative guidelines to reduce risk to human populations and to improve ecological sustainability associated with the higher volumes of stormwater and its associated run-off pollutants<sup>3,4</sup>.

Stormwater runoff from urban areas contains a variety of contaminants that can adversely impact receiving waters. Contaminants such as metals, pathogens and pesticides and nutrients (e.g. nitrogen and phosphorus) are common in runoff. Most stormwater runoff is discharged directly into freshwater and marine environments without any treatment. Only the portion of stormwater which enters the sewer network is treated in municipal wastewater treatment facilities. The intermittent presence of stormwater in combined urban sewer networks frequently results in overflows during or following significant storm events. The separation of stormwater from wastewater and on-site, decentralized stormwater runoff treatment can reduce pressures on urban infrastructure, mitigate flood risk and manage contaminant discharge to receiving waters. Filtration systems such as permeable reactive barriers and similar engineered structures for passive wastewater treatment are widely recognized as a cost-effective means of attenuating diffuse water pollution.

The results of filter material testing presented herein are based on experimental outcomes, discussions with StormFilter project WP2 participants during 2016 (especially regarding plans presented at Steering Groups #3 May 2016 and #4 October 2016), and on experimental plans distributed for comments in 2016. The information presented here concerns individual materials for potential use in stormwater filtration. These data will be complemented by additional investigation of these materials in layered systems in a summary report scheduled for delivery by the end of August 2017.

## 2. Contaminants in Stormwater Runoff

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Land use and anthropogenic activities largely dictate the nature and level of pollutants in stormwaters; however, contaminants such as sediments and dissolved and suspended particulates (total suspended solids, TSS), metals, nutrients, and organic chemicals are common in stormwater runoff<sup>5</sup>. Metals, including the metalloid arsenic, and substances which contribute to eutrophication of surface waters (in particular nitrogen and phosphorus) are among the main pollutants of concern listed in the EU Water Framework Directive<sup>6</sup>. Urban

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<sup>1</sup> Wahlgren, I., Kuismanen, K. & Makkonen, L. 2008. Ilmastomuutoksen huomioiminen kaavoituksessa – Tapaushkohtaisia tarkasteluja. Loppuraportti. VTT Tutkimusraportti VTT-R-03986-08.

<sup>2</sup> Population Reference Bureau: <http://www.prb.org/educators/teachersguides/humanpopulation/urbanization.aspx>

<sup>3</sup> HSY. 2010. Pääkaupunkiseudun ilmasto muuttuu. Sopeutumisstrategian taustaselvityksiä. HSY Helsingin seudun ympäristöpalvelut. HSY:n julkaisuja 3/2010. 92 p.

<sup>4</sup> Kuntaliitto, 2012. Hulevesiopas. 298 s.

<sup>5</sup> Makepeace, D.K., D.W. Smith and S.J. Stanley. 1995. *Critical Reviews in Environmental Science and Technology* 25:93-139.

<sup>6</sup> EU WFD. 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02000L0060-20140101>

stormwater runoff includes overland flows or drainage discharges from impervious surfaces as well as overland flows from public open spaces and green spaces, road verges, and construction sites (Table 1); road surfaces are the principal source and conveyor of pollutants in urban stormwater runoff<sup>7</sup>.

*Table 1. Pollutant sources, mean event concentrations and European Union, United States, and Australian environmental water quality standards (modified from Lundy et al.<sup>7</sup>).*

Pollutants & Sources	Event mean concentrations	EU water quality standards <sup>a, b</sup>	U.S. water quality standards <sup>c-e</sup>	AUS water quality standards <sup>f,g</sup>
<b>Nutrients (mg/L)</b>				
Sewer misconnections;	Total P: 0.02-39	Total P: 0.18	Total P: 0.008-0.128 <sup>c</sup>	Total P: 0.01-0.1 <sup>†</sup>
urban amenity fertilizer; residential;	Total N: 0.1-20	Total N: 5-65	Total N: 0.1-2.18 <sup>c</sup>	Total N: 0.12-1.5 <sup>f</sup>
highways, motorways & major roads; road gullies & pipe drains	NO <sub>3</sub> : 0.1-4.7 NH <sub>4</sub> : 0.2-3.8	NH <sub>4</sub> : 0.25-9 <sup>†</sup>		NO <sub>3</sub> : 700 <sup>g</sup> NH <sub>4</sub> : 0.006-0.1 <sup>f</sup>
<sup>†</sup> Depending on use				
<b>Metals (µg/L) NOTE: not including metal roofs</b>				
Highways, motorways & major roads; urban distributor roads; suburban roads; commercial estates; residential; roofs; road gullies & pipe drains	Cd: 0.2-13 Pb: 1-2410 Ni: 2-493 Zn: 53-3550	Cd: AA 0.08-0.25*; MAC 0.45-1.5* Pb: AA 7.2; MAC N/A Cu: 1-28* Ni: AA 20; MAC N/A Zn: 8-125*	Cd: CMC 2; CCC 0.25* <sup>d</sup> Pb: CMC 65; CCC 2.5* <sup>d</sup> Cu: variable, calculated via biotic ligand model Ni: CMC 470; CCC 52* <sup>d</sup> Zn: CMC & CCC 120* <sup>d</sup>	Cd: 0.2* <sup>†</sup> Pb: 3.4* <sup>f</sup> Cu: 1.4* <sup>f</sup> Ni: 11* <sup>f</sup> Zn: 8* <sup>f</sup>

\* Freshwater criteria vary depending on water hardness

<sup>a</sup> European Union environmental quality standards (EQSs) for priority and priority hazardous substances Cd, Pb, Ni<sup>8</sup>; UK EQSs for Cu, Zn<sup>9</sup>

<sup>b</sup> AA = annual average concentration; MAC = maximum allowable concentration

<sup>c</sup> Total P and Total N: Summary of Ecoregional Nutrient Criteria for freshwater systems<sup>9</sup>

<sup>d</sup> U.S. EPA Recommended Water Quality Criteria for freshwater aquatic life

<sup>e</sup> CMC = Criteria Maximum Concentration; CCC = Criteria Continuous Concentration

<sup>f</sup> Range of physical and chemical stressor default trigger values for slightly disturbed Australian ecosystems<sup>10</sup>

<sup>g</sup> Trigger values for 95% species protection in freshwater<sup>10</sup>

Metals are prevalent in urban dust and runoff, and are of particular concern in stormwater runoff due to their ubiquitous presence in urban and peri-urban areas, potential toxicity, and persistence in the environment. Vehicle traffic is a major source of metals, especially cadmium, copper, lead, nickel, and zinc<sup>11,12,13,14</sup>. The EU Water Framework Directive lists cadmium, lead and their respective compounds as priority substances, and cadmium is further identified as a priority hazardous substance. Cadmium is present in vehicle brake linings (2.7 mg/kg) and tire rubber (2.6 mg/kg), with wear rates for a standard vehicle equivalent to a cumulative 254 ng Cd/vehicle-km for brakes and tires<sup>7,15</sup>. Lead is present in brake linings and tires at much greater concentrations compared to cadmium; vehicle brake linings and tire rubber contain 3900 mg Pb/kg and 6.3 mg Cd/kg, respectively<sup>14</sup>. For a standard vehicle, wear rates equate to 551 ng Pb/vehicle-km<sup>7</sup>. Stormwater runoff from urban

<sup>7</sup> Lundy, L., J.B. Ellis, D.M. Revitt. 2012. *Water Research* 46:6589-6600.

<sup>8</sup> EU EQS. 2008. Directive 2008/105/EC. <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32008L0105>

<sup>9</sup> Comber, S.D.W., G. Merrington, L. Sturdy, K. Delbeke, F. Van Assche. 2008. *Science of the Total Environment* 403:12-22.

<sup>10</sup> ANZECC/ARMCANZ. 2000. Australian and New Zealand guidelines for fresh and marine water quality. [http://www.mincos.gov.au/publications/australian\\_and\\_new\\_zealand\\_guidelines\\_for\\_fresh\\_and\\_marine\\_water\\_quality](http://www.mincos.gov.au/publications/australian_and_new_zealand_guidelines_for_fresh_and_marine_water_quality)

<sup>11</sup> Barbosa, A.E., H.T. Jacobsen. 1999. *Science of the Total Environment* 235:151-159.

<sup>12</sup> Gill, L.W., P. Ring, N.M.P. Higgins, P.M. Johnston. 2014. *Ecological Engineering* 70:133-139.

<sup>13</sup> Granier, L., M. Chevreuil, A.-M. Carru, R. Létolle. 1990. *Chemosphere* 21(9):1101-1107.

<sup>14</sup> Westerlund, C., M. Viklander, M. Bäckström. 2003. *Water Science and Technology* 48(9):93-101.

<sup>15</sup> Legret, M., C. Pagotto. 1999. *Science of the Total Environment* 235:143-150.



roads exhibits higher event mean concentration values for cadmium and lead relative to rural roads due to high annual daily average traffic flow in urban areas.

Chemical fertilizers applied to lawns, gardens, public open spaces, golf courses, and other areas within urban and peri-urban catchments are major contributors to nutrient loads in stormwater runoff<sup>16,17,18,19</sup>. Excessive inputs of nutrients to coastal waters can result in the development of hypoxic zones. Hypoxic zones can occur naturally in coastal marine areas; however, anthropogenic activities during the previous 50 years have resulted in a dramatic increase in the magnitude and extent of hypoxic coastal zones around the world<sup>20</sup>.

Marine hypoxic or “dead zones” develop as a result of nitrogen and phosphorus enrichment of coastal waters. The quantity of reactive nitrogen and phosphorus currently released to the world’s oceans is three times greater than emissions during pre-industrial times<sup>21,22</sup>. The abundant supply of nutrients causes a tremendous increase in net primary productivity by phytoplankton and other autotrophs (eutrophication). When the autotrophs die they sink to the bottom and are decomposed by bacteria, resulting in reduced oxygen levels. As winds move surface waters away from the coastline the hypoxic deeper layers are brought to the surface creating a dead zone. As of 2010, 415 eutrophic and hypoxic coastal systems, “dead zones”, were identified worldwide (Figure 1). Attenuation of nutrients in aqueous discharges from urban areas is essential to protect or restore coastal marine ecosystems.

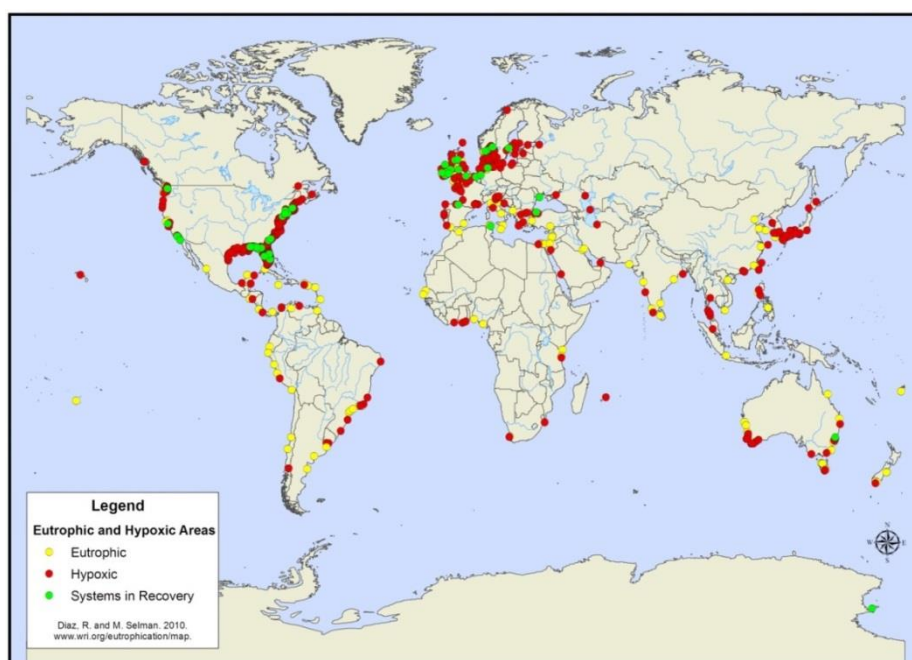


Figure 1. Eutrophic and hypoxic marine areas as of 2010 (image: [www.wri.org](http://www.wri.org)).

<sup>16</sup> Chessman, B.C., P.E. Hutton, J.M. Burch. 1992. *Freshwater Biology* 28:349-361.

<sup>17</sup> Garn, H.S. 2002. *USGS Water Resources Investigations Report 02-4130*.

<sup>18</sup> Steuer, J., W. Selbig, N. Hornewer, J. Prey. 1997. *U.S. Geological Survey Water-Resources Investigations Report 97-4242*.

<sup>19</sup> Wernick, B.B.G., K.E. Cook, H. Schreier. 1998. *Journal of the American Water Resources Association* 34(3):639-650.

<sup>20</sup> Rabatyagov, S.S., C.L. Kling, P.W. Gassman, N.N. Rabalais, R.E. Turner. 2014. *Review of Environmental Economics and Policy* 8:58-79.

<sup>21</sup> Rabalais, N.N., R.J. Diaz, L.A. Levin, R.E. Turner, D. Gilbert, J. Zhang. 2010. *Biogeosciences* 7:585-619.

<sup>22</sup> Turner, R.E., N.N. Rabalais, D. Justić. 2012. *Marine Pollution Bulletin* 64:319-324.

### 3. Filter Material pH and Electrical Conductivity

The pH and EC of filter materials are easily-measured parameters which provide important information about a material's potential for use in water filtration schemes. In particular, pH is considered a 'master variable' with respect to the behavior of elements in soils and aquatic systems because pH is intimately associated with chemical, biochemical and biological processes in the environment. The chemical form that an element takes in solution is key to its behavior. Both metallic and non-metallic elements may occur in different oxidation states and in soluble complexes with different organic or inorganic ions or molecules. The formation of soluble complexes between elements in stormwater and dissolved  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  or organic molecules such as humic or fulvic acids increases the elements' total solubility<sup>23</sup>.

The oxidation state of pollutant elements was not specifically addressed in the present study due to the short hydraulic retention time of stormwater within filtration structures (e.g. columns in experimental trials).

Ten different mineral- and bio-based filter materials were received from StormFilter project partners along with descriptions of each material. Initial filter material characterization included measurements of pH and electrical conductivity (EC). For each filter material, the pH and EC were measured in a 1:5 aqueous extract using deionized water. The filter material pH was also measured in 0.01 M  $\text{CaCl}_2$  (1:5 solid to liquid ratio), because pH measured in dilute  $\text{CaCl}_2$  ( $\text{pH}_{\text{CaCl}_2}$ ) is more stable and reproducible than pH determined in aqueous solution ( $\text{pH}_{\text{H}_2\text{O}}$ )<sup>24</sup>.

Table 2. Basic characteristics of filter materials examined in the StormFilter project.

Material	Description	$\text{pH}_{\text{H}_2\text{O}}$	$\text{pH}_{\text{CaCl}_2}$	EC (mS/cm)
<b>KaM 0/5</b>	Crushed & screened rock fines, 0–5 mm	$9.3 \pm 0.1$	$8.2 \pm 0.1$	$0.038 \pm 0.002$
<b>SSr 0/16</b>	Screened sand, 0–16 mm	$7.3 \pm 0.1$	$6.8 \pm 0.1$	$0.009 \pm 0.001$
<b>Leca 2–4 mm round</b>	Expanded clay aggregate; round & crushed mixture, 2–4 mm	$10.3 \pm 0.1$	$9.3 \pm 0.2$	$0.085 \pm 0.004$
<b>Leca 0–3 mm crushed</b>	Expanded clay aggregate; crushed, flat & multi-angular, 0–3 mm	$10.8 \pm 0.2$	$10.3 \pm 0.3$	$0.197 \pm 0.053$
<b>Leca 3–8 mm crushed</b>	Expanded clay aggregate; crushed, flat & multi-angular, 3–8 mm	$10.1 \pm 0.2$	$9.2 \pm 0.3$	$0.083 \pm 0.005$
<b>Filtralite® P 0.5–4 mm</b>	Expanded clay aggregate; crushed, flat & multi-angular, 0.5–4 mm	$10.1 \pm 0.0$	$8.0 \pm 0.2$	$0.389 \pm 0.014$
<b>Peat</b>	Peat	$4.3 \pm 0.1$	$3.5 \pm 0.0$	$0.071 \pm 0.001$
<b>Peat + 10% limestone</b>	90 wt.% peat + 10 wt.% crushed limestone ( $\text{CaCO}_3$ )	$4.6 \pm 0.1$	$4.4 \pm 0.3$	$0.084 \pm 0.001$
<b>Birch biochar</b>	Powder (<25 mesh) biochar from birch wood	$9.8 \pm 0.0$	$8.7 \pm 0.0$	$2.703 \pm 0.444$
<b>Spruce biochar</b>	Chip (3-25 mm) biochar from spruce wood	$8.3 \pm 0.2$	$7.8 \pm 0.1$	$0.156 \pm 0.030$

Although all mineral- and bio-based filter materials were from natural sources, several exhibited pH outside the pH 5.0–8.5 range typically considered acceptable range for plant growth and soil microbial activity<sup>23</sup>. Both peat and peat + 10% limestone had pH <5.0 in 1:5 aqueous extracts. In contrast, many of the filter materials, including KaM 0/5, Leca 2–4 mm round, Leca 0–3 mm crushed, Leca 3–8 mm crushed, Filtralite® P 0.5–4 mm, and birch biochar exhibited pH >8.5. These results highlight the importance of monitoring effluent pH in filter material experiments. The EC of all 1:5 filter material aqueous extracts were <4 mS/cm and acceptable for environmental use<sup>23</sup>.

<sup>23</sup> McBride, M.B. 1994. Environmental Chemistry of Soils. Oxford University Press, New York.

<sup>24</sup> Rayment, G.E. and Higginson, F.R. (1992) Australian Laboratory Handbook of Soil and Water Chemical Methods. Inkarta Press, Melbourne.

## 4. Laboratory Batch Testing of Material Pollutant Removal Capacity

The mobility of elements in solution can be decreased by filtering through a chemically reactive solid material with a large number of surface sorption sites, or which creates a chemical environment favorable to precipitation of the element. In soil, most trace elements have low mobility because they adsorb strongly to soil minerals and organic matter, or form insoluble precipitates. Stormwater filtration schemes build upon knowledge of ion interactions with mineral and organic phases in soil to design systems with the capacity to effectively remove elements from solution through sorption and/or precipitation reactions. The capacity of a filter material to remove contaminant elements from solution provides an indication of its useful lifespan.

In this study, the capacity of each selected filter material to remove selected common stormwater contaminant ions from water was determined using a synthetic solution representative of a 'first flush' of stormwater following a prolonged dry period (See Appendix I, Table 3). Sub-samples (0.135 kg) of each test material were mixed with 1.35 L of synthetic stormwater in 1.5 L polypropylene bottles. Solutions were placed on a reciprocal mixer for 24 h, then filtered to 0.45 µm and supernatants analyzed to assess pollutant removal by each material in a 1:10 solid to liquid mixture at thermodynamic equilibrium.

Table 3. StormFilter project nominal synthetic stormwater composition used in material batch testing.

Pollutant	Nominal Concentration (µg/l)
<b>Cu</b>	500
<b>Pb</b>	1 000
<b>Zn</b>	2 000
<b>Total P</b>	500
<b>Cl</b>	100 000
<b>SO<sub>4</sub></b>	80 000
<b>Organic C</b>	10 000

All of the materials tested showed some ability to remove copper (Figure 2), lead (Figure 3) and zinc (Figure 4), with the exception of the KaM 0/5 crushed rock aggregate which did not remove lead from the synthetic stormwater.

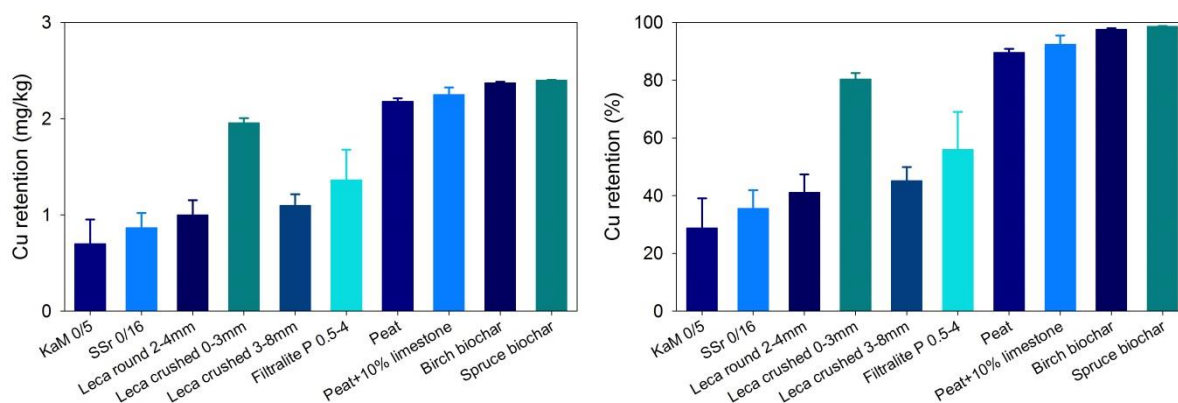


Figure 2. Copper (Cu) retention by selected materials in 1:10 solid to stormwater solution batch test, expressed in mg/kg (left) and as per cent of total (right). Error bars indicate standard deviation of triplicate measurements.

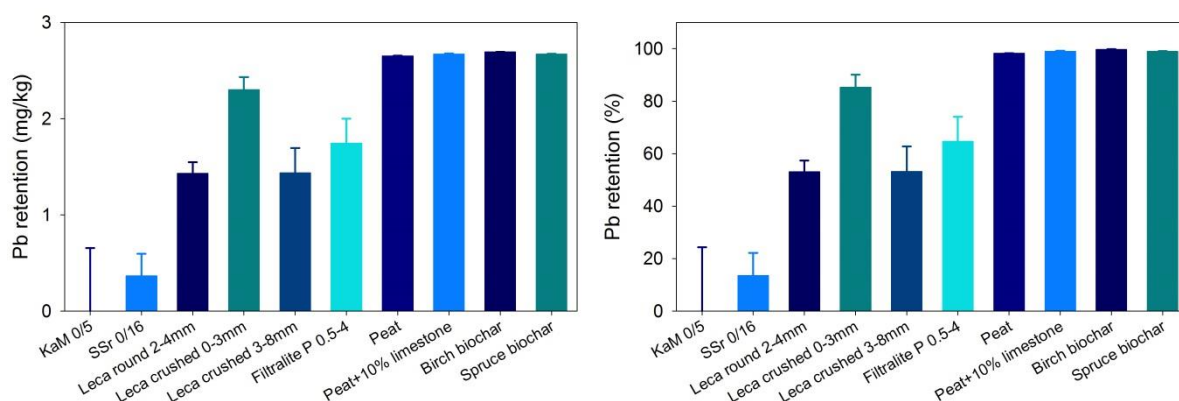


Figure 3. Lead (Pb) retention by selected materials in 1:10 solid to stormwater solution batch test, expressed in mg/kg (left) and as per cent of total (right). Error bars indicate standard deviation of triplicate measurements.

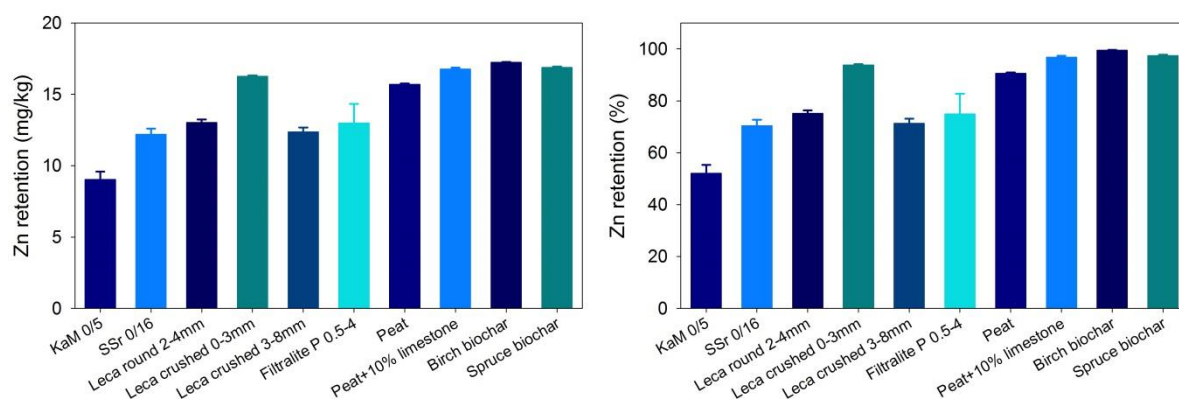


Figure 4. Zinc (Zn) retention by selected materials in 1:10 solid to stormwater solution batch test, expressed in mg/kg (left) and as per cent of total (right). Error bars indicate standard deviation of triplicate measurements.

Similarly, nearly all materials examined showed capacity for phosphorus removal from solution (Figure 5). Exceptions included KaM 0/5 crushed rock aggregate which exhibited negligible phosphorus removal, and the birch biochar which released phosphorus from the solid phase into solution. The observed increase in phosphorus concentration is expressed in Table 4 by a negative value.

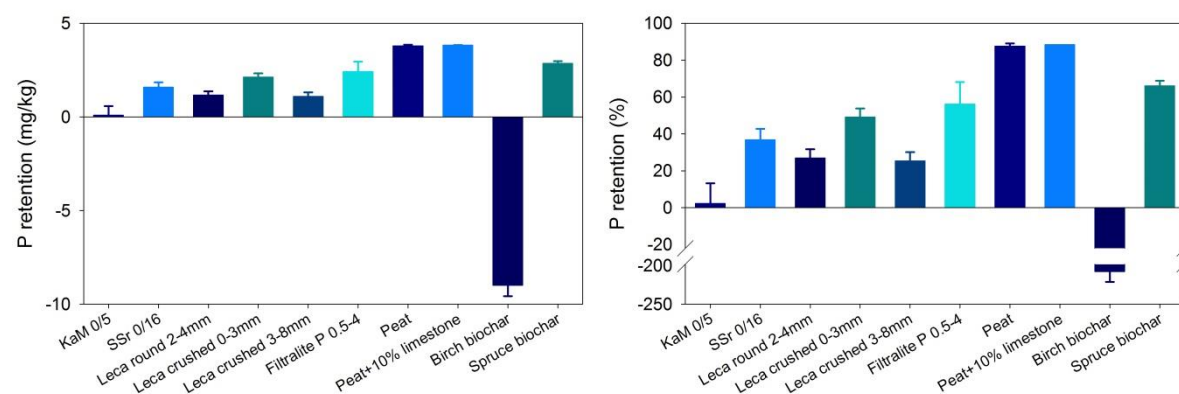


Figure 5. Phosphorus (P) retention by selected materials in 1:10 solid to stormwater solution batch test, expressed in mg/kg (left) and as per cent of total (right). Error bars indicate standard deviation of triplicate measurements.

In general, none of the materials tested showed substantial capacity for  $\text{SO}_4^{2-}$  (Figure 6) or  $\text{Cl}^-$  (Figure 7) removal, and in fact released some  $\text{SO}_4^{2-}$  and/ or  $\text{Cl}^-$  into solution. Increases in  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  concentration relative to initial synthetic stormwater, representing a net release of  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$ , are expressed in Table 4 by negative values. The aggregate materials SSr 0/16 and KaM 0/5 each retained nearly 13 mg  $\text{SO}_4^{2-}$ /kg whilst the Leca 3–8 mm crushed and Filtralite® P 0.5–4 mm materials retained ca. 21 and 90 mg  $\text{Cl}^-$ /kg, respectively.

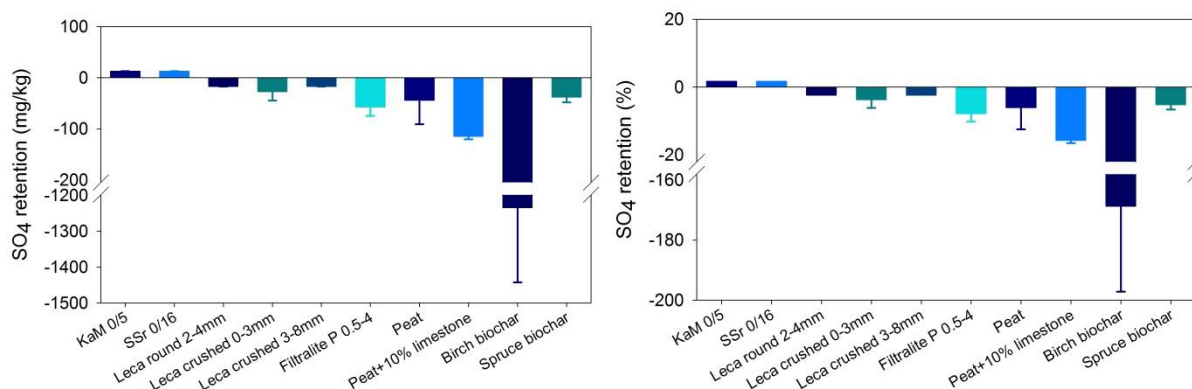


Figure 6. Sulfate ( $\text{SO}_4^{2-}$ ) retention or release by selected materials in 1:10 solid to stormwater solution batch test, expressed in mg/kg (left) and as per cent of total (right). Error bars indicate standard deviation of triplicate measurements.

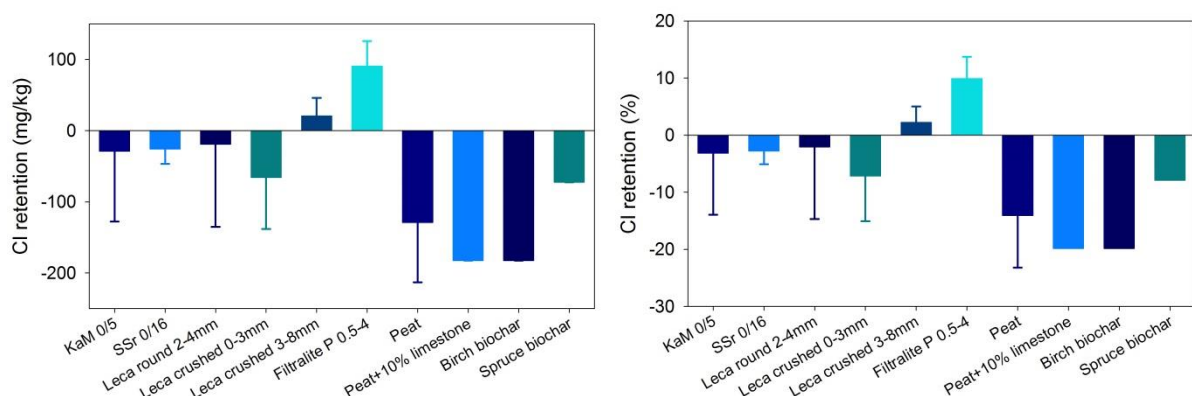


Figure 7. Chloride ( $\text{Cl}^-$ ) retention or release by selected materials in 1:10 solid to stormwater solution batch test, expressed in mg/kg (left) and as per cent of total (right). Error bars indicate standard deviation of triplicate measurements.

Note that contaminant sorption capacities determined via batch tests are concentration-dependent. The net removal of a given contaminant ion represents the maximum potential removal of that ion at the concentration tested and in a static system without constant replenishment of solution. The partitioning of the ion between the solid surface and the water represents both the affinity of the solid surface for that ion as well as the thermodynamic equilibrium between sorbed (surface-associated) and ‘free’ (in solution) ions. Thus, if the materials above were tested using a more concentrated solution, i.e. an aqueous solution representative of metalliferous mine process water, we would likely observe greater sorption of each ion/ higher sorption capacities. The sorption capacities shown herein are indicative of the relative affinity of each solid material for the selected ions in a dilute solution representative of stormwater. Pollutant removal capacities for the tested materials at a 1:10 solid to liquid ratio are summarized in Table 4.



Table 4. Pollutant removal (mg/kg) by each filter material as determined in laboratory batch tests. Results represent mean of triplicate samples  $\pm$  one standard deviation from the mean. Negative values indicate net release of the respective ion. <sup>†</sup>

	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	PO <sub>4</sub> <sup>3-</sup> /P <sup>5+</sup>
	Removal, mg/kg					
KaM 0-5	12.7 $\pm$ 0.0	-29.2 $\pm$ 98.6	0.7 $\pm$ 0.3	0.0 $\pm$ 0.7	9.0 $\pm$ 0.6	0.1 $\pm$ 0.5
SSr 0-16	12.7 $\pm$ 0.0	-25.8 $\pm$ 20.8	0.9 $\pm$ 0.2	0.4 $\pm$ 0.2	12.2 $\pm$ 0.4	1.6 $\pm$ 0.3
Leca 0-3 crushed	-27.2 $\pm$ 17.3	-65.8 $\pm$ 72.3	2.0 $\pm$ 0.0	2.3 $\pm$ 0.1	16.3 $\pm$ 0.1	2.1 $\pm$ 0.2
Leca 2-4 round	-17.2 $\pm$ 0.0	-19.2 $\pm$ 116	1.0 $\pm$ 0.2	1.4 $\pm$ 0.1	13.0 $\pm$ 0.2	1.2 $\pm$ 0.2
Leca 3-8 crushed	-17.2 $\pm$ 0.0	20.8 $\pm$ 25.2	1.1 $\pm$ 0.1	1.4 $\pm$ 0.3	12.4 $\pm$ 0.3	1.1 $\pm$ 0.2
Filtralite® P 0,5-4	-57.2 $\pm$ 17.3	90.8 $\pm$ 35.1	1.4 $\pm$ 0.3	1.7 $\pm$ 0.3	13.0 $\pm$ 1.3	2.4 $\pm$ 0.5
Peat	-44.2 $\pm$ 46.7	-129 $\pm$ 83.9	2.2 $\pm$ 0.0	2.7 $\pm$ 0.0	15.7 $\pm$ 0.1	3.8 $\pm$ 0.1
Peat + 10 wt.% limestone	-115 $\pm$ 5.8	-183 $\pm$ 0.0	2.2 $\pm$ 0.1	2.7 $\pm$ 0.0	16.8 $\pm$ 0.1	3.8 $\pm$ 0.0
Birch biochar	-1234 $\pm$ 208	-183 $\pm$ 0.0	2.4 $\pm$ 0.0	2.7 $\pm$ 0.0	17.2 $\pm$ 0.0	-9.0 $\pm$ 0.6
Spruce biochar	-38.2 $\pm$ 10.0	-72.5 $\pm$ 0.0	2.4 $\pm$ 0.0	2.7 $\pm$ 0.0	16.9 $\pm$ 0.1	2.9 $\pm$ 0.1

<sup>†</sup> Blue text highlights values which indicate net retention  $\geq$ 50% of total ion in solution. Red text highlights negative values indicative of net release of the respective ion.

## 5. Laboratory Column Testing of Pollutant Removal

### 5.1 Column Trials Using 1X Concentrated Synthetic Stormwater

Experimentation with various column configurations led to the design shown below (Figure 8). The “reactive” or test material in each column was placed between layers of aggregate, including 40 mm of coarse aggregate and 200 mm of SSr 0/16 medium-fine aggregate, to normalize hydraulic retention time between materials with widely varying hydraulic conductivity. The aggregate layers served to slow the flow of synthetic stormwater in highly porous materials with low hydraulic retention time.

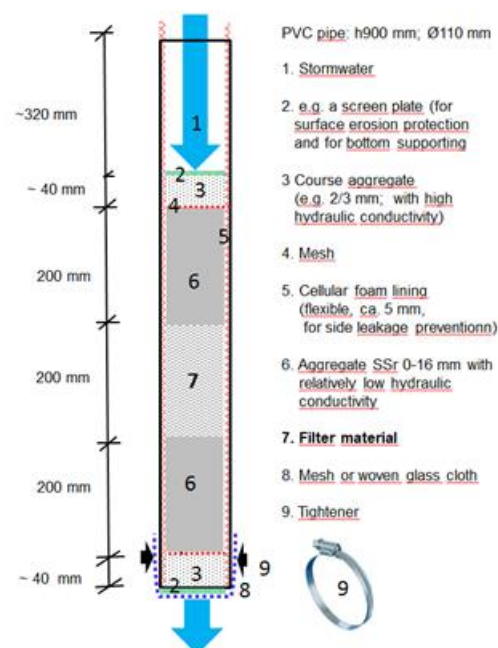


Figure 8. Configuration of StormFilter laboratory test columns for investigation of a single reactive phase, indicated here as no. 7.



Hydraulic retention time is effectively the time during which the water remains in contact with the solid phase. Thus, hydraulic retention time determines the time allowed for reaction between the solid material(s) and pollutants in the water. A hydraulic retention time of 1 hour was targeted, assuming a total hydraulic retention time of 1 hour would allow approximately 20 minutes contact time between the test solid material and influent stormwater.

The observed variation in hydraulic retention time between columns containing different test materials (Figure 9) is due to differences among the respective hydraulic conductivities of each material, or how easily water is able to pass through each material. The hydraulic conductivity is, in turn, dependent upon factors such as grain size of the solid material, the size and shape of pore spaces within the solid matrix, total porosity of the solid matrix, and the total surface area of the solid material per unit mass (known as the specific surface area).

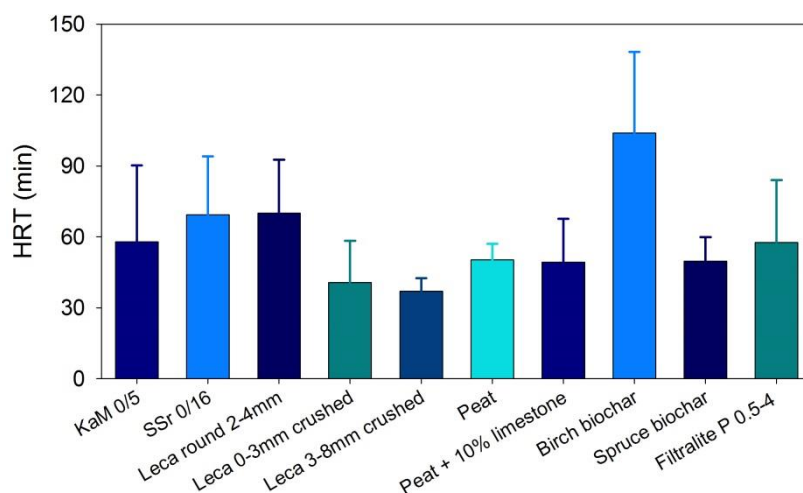


Figure 9. Mean hydraulic retention time (HRT) in each StormFilter laboratory column. Error bars indicate standard deviation of triplicate measurements.

Similar to the results of laboratory batch tests, none of the materials tested showed substantial sulfate ( $\text{SO}_4^{2-}$ ) or chloride ( $\text{Cl}^-$ ) retention during the column trial (Figure 10, Figure 11). All materials examined effectively removed copper (Figure 12), lead (Figure 13) and zinc (Figure 14) from the synthetic stormwater solution.

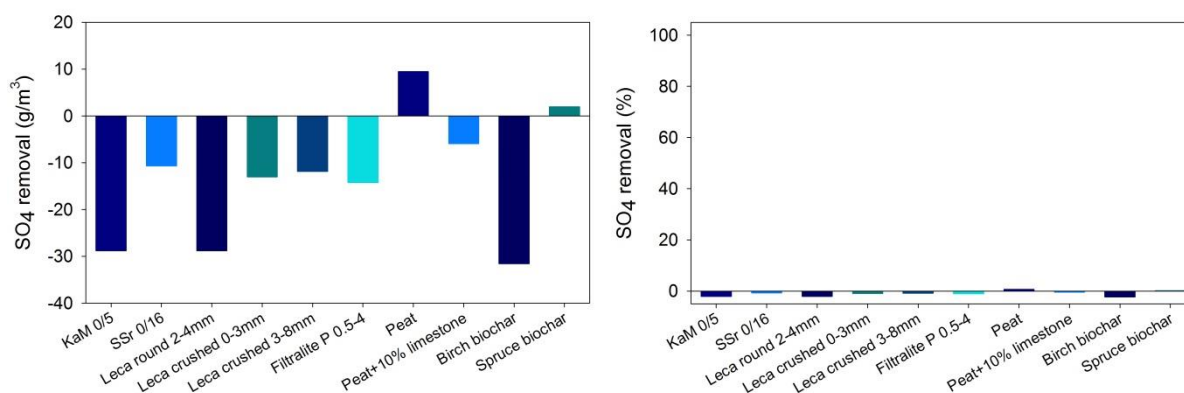


Figure 10. Overall sulfate ( $\text{SO}_4^{2-}$ ) retention or release by filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

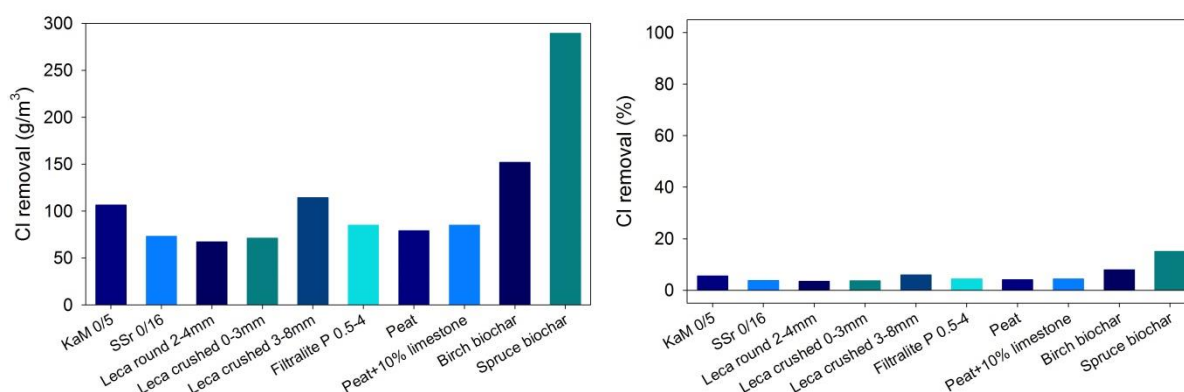


Figure 11. Overall chloride (Cl⁻) retention by filter materials in flow-through column testing, expressed in g/m³ (left) and as per cent of total (right).

Metal attenuation by each filter material in the column test differed from results of batch testing. Copper (Figure 12), lead (Figure 13) and zinc (Figure 14) removal from influent stormwater in column tests was greater than the respective proportion of each metal removed in the batch test.

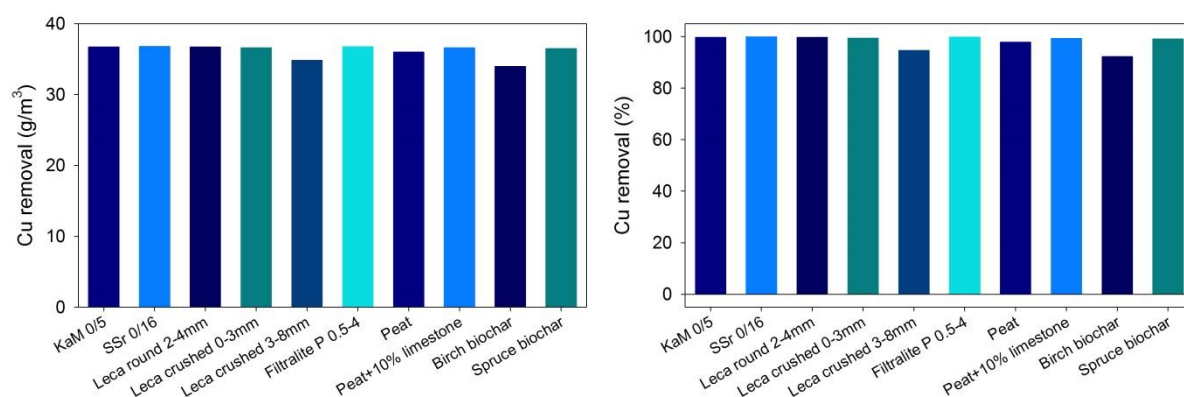


Figure 12. Overall copper (Cu) retention by filter materials in flow-through column testing, expressed in g/m³ (left) and as per cent of total (right).

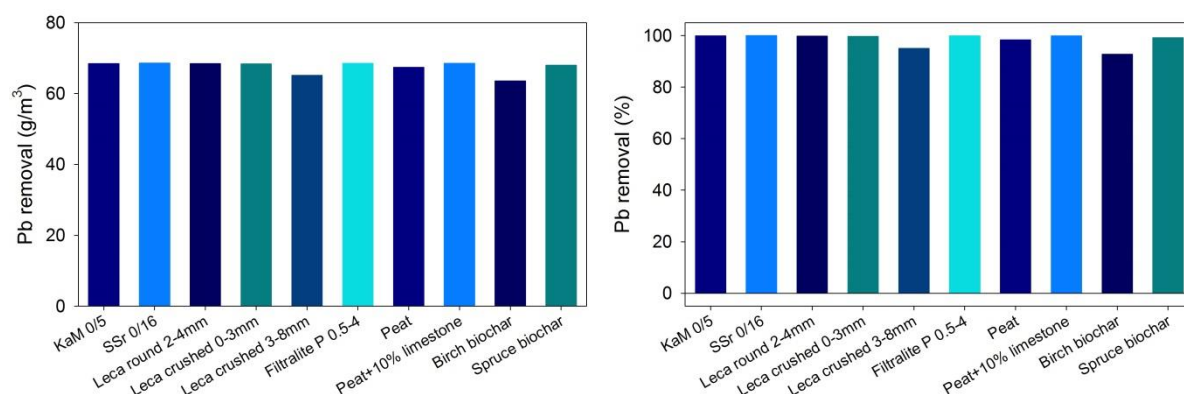


Figure 13. Overall lead (Pb) retention by filter materials in flow-through column testing, expressed in g/m³ (left) and as per cent of total (right).

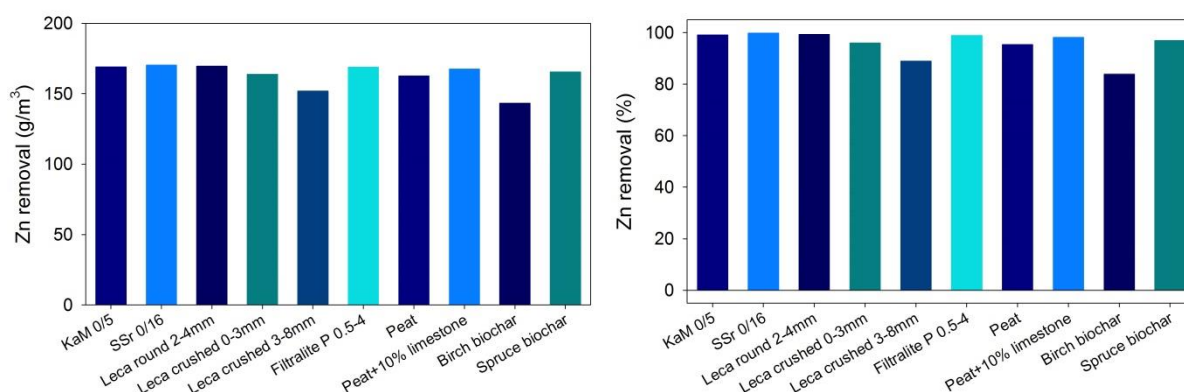


Figure 14. Overall zinc (Zn) retention by filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

Phosphorus removal from influent stormwater in the column experiment was substantially greater than the phosphorus sorption capacity observed in batch testing. With the exception of the birch biochar, all materials demonstrated effective removal of phosphorus (Figure 15). The birch biochar initially showed a net release of phosphorus, observed as a small net increase in phosphorus concentration in effluent relative to influent stormwater. Phosphorus retention by the birch biochar increased as the concentration of influent stormwater phosphorus increased, however, resulting in net phosphorus removal from influent solution.

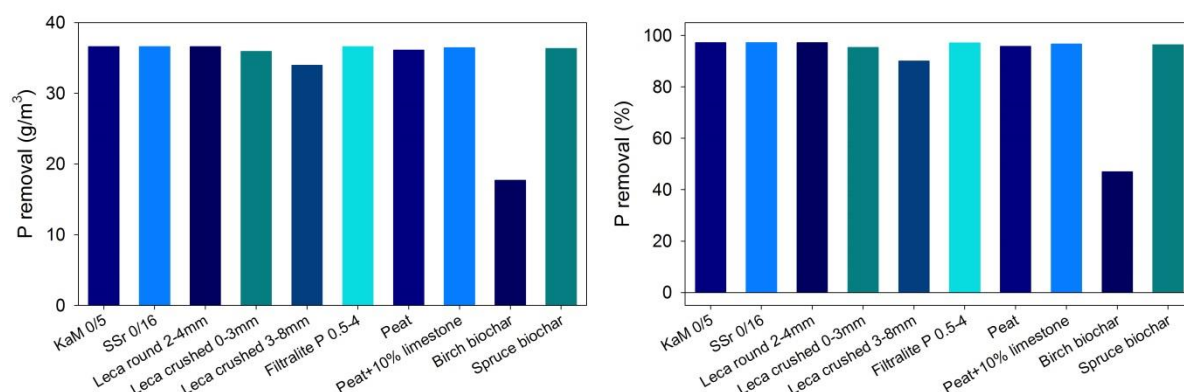


Figure 15. Overall phosphorus (P) retention by filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

The figures above show overall pollutant retention by each material after passage of 40.5 L of synthetic stormwater solution through each respective filter material. After the addition of 33 L synthetic stormwater to each column, there was no indication of decreasing metal and phosphorus removal by the test materials. This result indicates that an appropriately sized structure employing any of the materials tested as reactive filtration media would be expected to effectively remove copper, lead and zinc from influent stormwater in the near term (e.g.  $\leq 3$  years). In addition, any of the materials tested as reactive filtration media, with the exception of birch biochar, could be expected to effectively remove phosphorus from influent stormwater in the near term. The birch biochar could be expected to initially release phosphorus, followed by net phosphorus sorption. This result limits the application of birch biochar as filtration media to areas unlikely to be negatively impacted by a slight increase in surface water phosphorus concentration.

After the addition of 33 L synthetic stormwater to each test column in 12 additions of 1.5 L each, the concentrations of metals and phosphorus in the influent stormwater were increased twenty-fold (20X; see Table 5). The decision to accelerate stormwater treatment simulation in

the column trial was an attempt to estimate longer-term material performance during the term of the StormFilter project. Results obtained following the addition of 3 L (2 x 1.5 L) and 7.5 L (2 x 1.5 L) of the 20X concentrated synthetic stormwater, after x-axis point 36 L in the following figures, show a general decrease in the affinity for zinc among all materials tested and a lesser general increase in phosphorus concentration in column effluents.

*Table 5. StormFilter project nominal synthetic stormwater composition used in laboratory testing.*

Pollutant	1X Nominal Concentration (µg/L)	20X Nominal Concentration (µg/L)
<b>Cu</b>	500	10 000
<b>Pb</b>	1 000	20 000
<b>Zn</b>	2 000	40 000
<b>Total phosphorus</b>	500	10 000
<b>Cl</b>	100 000	140 000
<b>SO<sub>4</sub></b>	80 000	94 000
<b>Organic carbon</b>	10 000	10 000

Additional organic carbon was not added to the 20X concentrated stormwater (Table 5). Because neither chloride nor sulfate were effectively attenuated by any of the materials in either batch testing or column testing from 0–33 L, further investigation focused on metals and phosphorus only. Chloride and sulfate were not quantified in column effluents after analysis of the 33 L effluents (e.g., Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in effluents from columns were not quantified at 36 L or 40.5 L).

A total of 7 x 1.5 L aliquots of 20X concentrated stormwater were added to each test column, yielding a total addition of 40.5 L to each column containing a single test material. The first 33 L of added stormwater were the “regular” 1X concentration representative of first flush stormwater, whereas the remaining 7.5 L were the 20X concentrated solution. In effect, the addition of 7.5 L at a 20X concentration simulates the addition of 150 L of “regular” 1X concentration stormwater. The results for each material shown on the following pages therefore represent the net treatment of 183 L of first flush stormwater by each 0.002 m<sup>3</sup> of material, or 96 331 L stormwater/m<sup>3</sup> filter material.

Detailed plots in the following sub-sections show stormwater influent and column effluent pH, and concentrations of analytes sulfate (SO<sub>4</sub><sup>2-</sup>), chloride (Cl<sup>-</sup>), copper (Cu<sup>2+</sup>), lead (Pb<sup>2+</sup>), zinc (Zn<sup>2+</sup>) and phosphorus (P<sup>5+</sup>, present as phosphate PO<sub>4</sub><sup>3-</sup>) in each respective column effluent as a function of time (expressed as effluent flux). In each of the following plots, the vertical dashed line at 33 L influent represents the change from ‘normal’ 1X concentration synthetic stormwater to the 20X concentrated synthetic stormwater influent solution.

### 5.1.1 Aggregate filter materials

The pH of effluents from experimental columns containing aggregates KaM 0/5 and SSr 0/16 were slightly alkaline at pH 7-8, and remained above pH 7 when influent stormwater pH decreased to ca. 6 (Figure 16). This indicates that the aggregate materials possess some acid neutralization capacity.

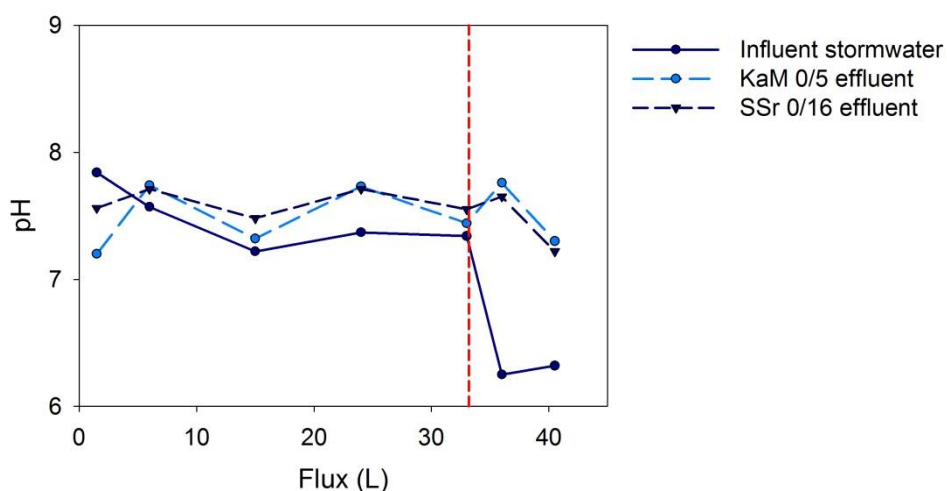


Figure 16. Influent stormwater pH and pH of effluents from columns containing aggregate filter materials.

Both KaM 0/5 and SSr 0/16 initially exhibited removal of sulfate from synthetic stormwater (Figure 17). With further addition of stormwater to experimental columns, however, the initially sorbed sulfate was gradually removed. Thus, there was zero net sulfate removal from influent stormwater by either KaM 0/5 or SSr 0/16 aggregate materials. The SSr 0/16 aggregate exhibited slight initial retention of chloride from influent stormwater followed by partial desorption (Figure 18), whilst KaM 0/5 aggregate continued to retain the small quantity of chloride initially retained.

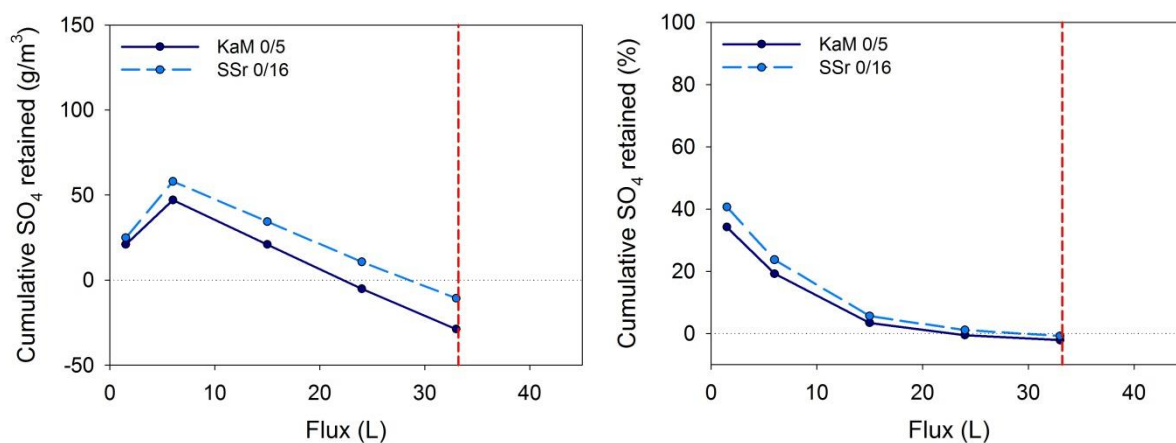


Figure 17. Cumulative sulfate ( $\text{SO}_4^{2-}$ ) retention or release by aggregate filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left), and as per cent of total (right).

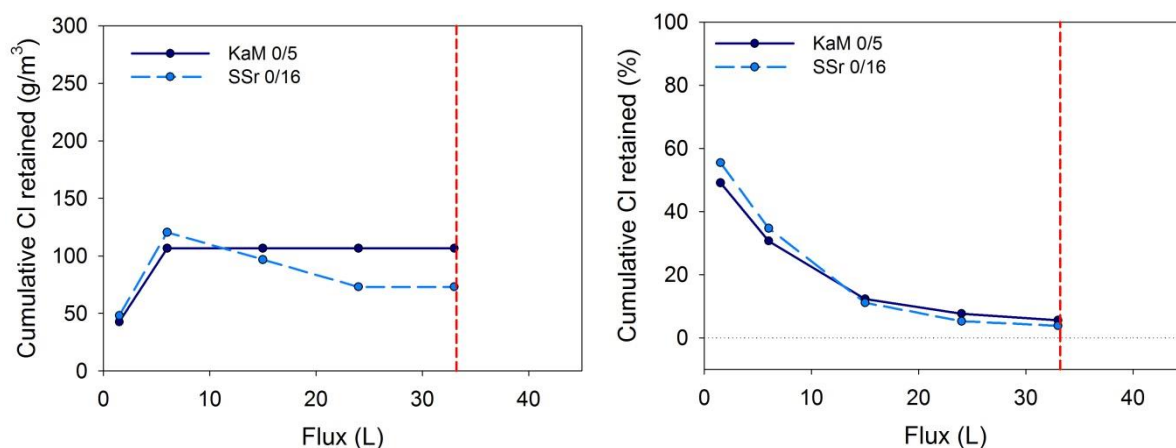


Figure 18. Cumulative chloride (Cl) retention by aggregate filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

Copper (Figure 19), lead (Figure 20) and zinc (Figure 21) were all effectively removed from influent stormwater and retained by both KaM 0/5 and SSr 0/16 aggregate filter materials. Lead and zinc are all classified as soluble, strongly cations which are considered exchangeable and somewhat mobile<sup>22</sup>. Primary silicate mineral surfaces are substantially less chemically reactive than secondary layer silicates or oxide/oxyhydroxide minerals; however, the alkaline pH of the KaM 0/5 and SSr 0/16 aggregates used in the present study indicates the presence of secondary carbonate minerals within the aggregate matrix. Carbonate minerals are known to effectively remove metals and phosphorus from solution through a combination of ion exchange and precipitation on the carbonate mineral surface<sup>25,26</sup>. Approximately 99% of the cumulative copper, lead and zinc were removed from influent stormwater by both KaM 0/5 and SSr 0/16.

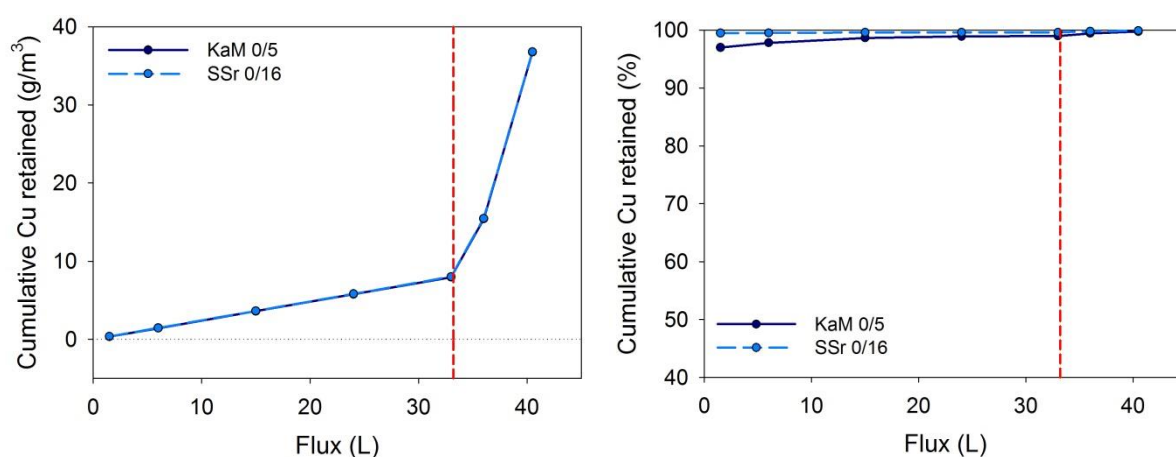


Figure 19. Cumulative copper (Cu) retention by aggregate filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

<sup>25</sup> Zachara, J.M., Cowan, C.E., Resch, C.T. 1991. *Geochimica et Cosmochimica Acta* 55(6):1549-1562.

<sup>26</sup> Wendling, L.A., Blomberg, P., Sarlin, T., Priha, O., Arnold, M. 2013. *Applied Geochemistry* 37:1587-169.



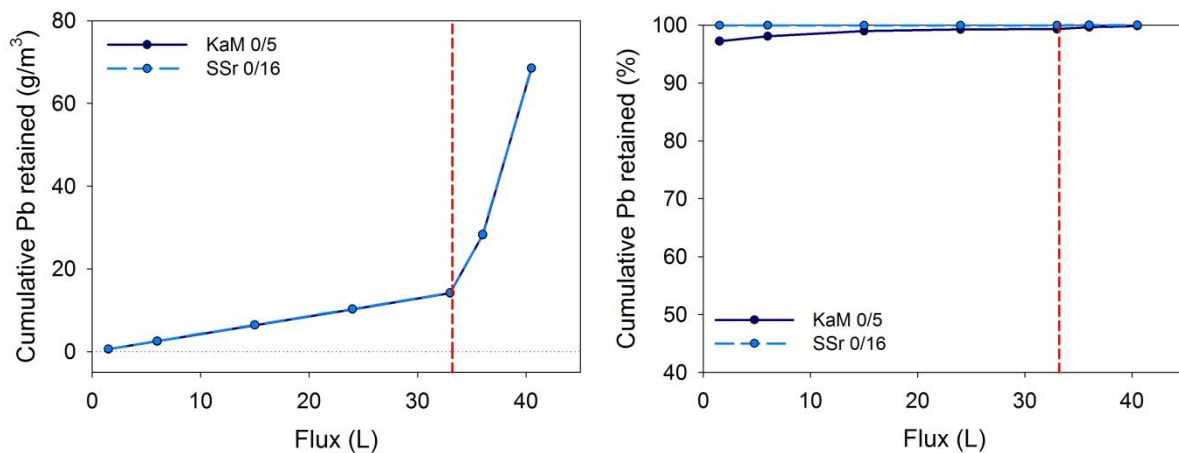


Figure 20. Cumulative lead (Pb) retention by aggregate materials in column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

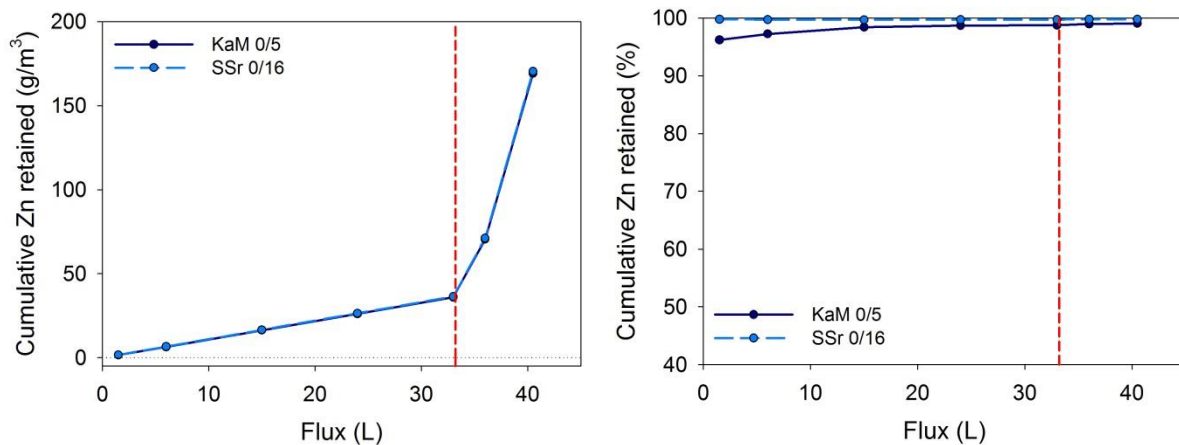


Figure 21. Cumulative zinc (Zn) retention by aggregate filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

Figure 22 shows cumulative phosphorus retention by KaM 0/5 and SSr 0/16 aggregates as a function of influent volume. The apparent increase in per cent (%) phosphorus retention when the influent concentration was increased twenty-fold is partially an artefact of experimental conditions. The 1X concentrated synthetic stormwater contained nominally  $500 \mu\text{g P/L}$ , and the analytical limit of detection was  $50 \mu\text{g P/L}$ . Where the measured concentration of phosphorus was less than the analytical limit of detection, a concentration equal to the limit of detection ( $50 \mu\text{g/L}$ ) was assumed for calculation purposes. Thus, the maximum phosphorus attenuation was  $\sim 90\%$  in 1X concentrated stormwater. When the concentration of pollutants in stormwater was increased to a nominal 20X concentration, effluent could be diluted prior to analysis and it was possible to observe greater than 90% removal of phosphorus by filter materials.

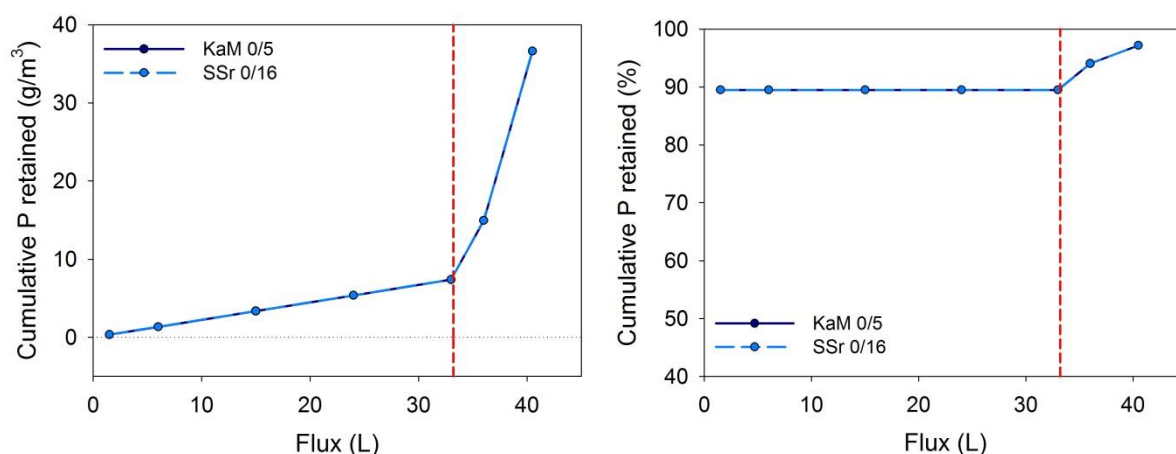


Figure 22. Cumulative phosphorus (P) retention by aggregate filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

### 5.1.2 Leca® and Filtralite® filter materials

Similar to the KaM 0/5 and SSr 0/16 aggregate materials, the pH of effluents from experimental columns containing Leca and Filtralite® products were slightly alkaline at pH 7–8, and remained above pH 7 when influent stormwater pH decreased to ca. 6 (Figure 23). Although the pH of Leca and Filtralite® products in deionized water (1:5 solid to liquid ratio) ranged from 10.1 to 10.8, the pH of filtered stormwater effluent from columns containing Leca and Filtralite® products remained less than ca. pH 8.

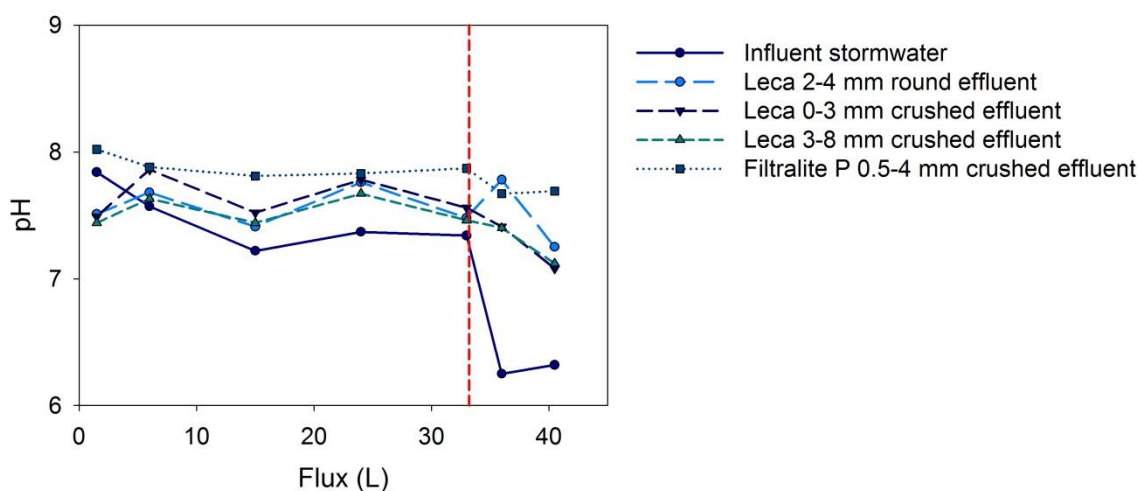


Figure 23. Influent stormwater pH and pH of effluents from columns containing Leca and Filtralite® products.

All the Leca and Filtralite® products examined initially removed some sulfate from synthetic stormwater (Figure 24). As observed with the KaM and SSr aggregates, the sulfate initially sorbed by Leca and Filtralite® products was gradually removed from the mineral surface with further addition of stormwater to experimental columns. Thus, there was zero net sulfate removal from influent stormwater by Leca or Filtralite® products. The Leca and Filtralite® products showed slight initial retention of chloride from influent stormwater followed by partial desorption (Figure 25), with the exception of the Leca 3–8 mm crushed material which continued to retain the small quantity of chloride initially sorbed.

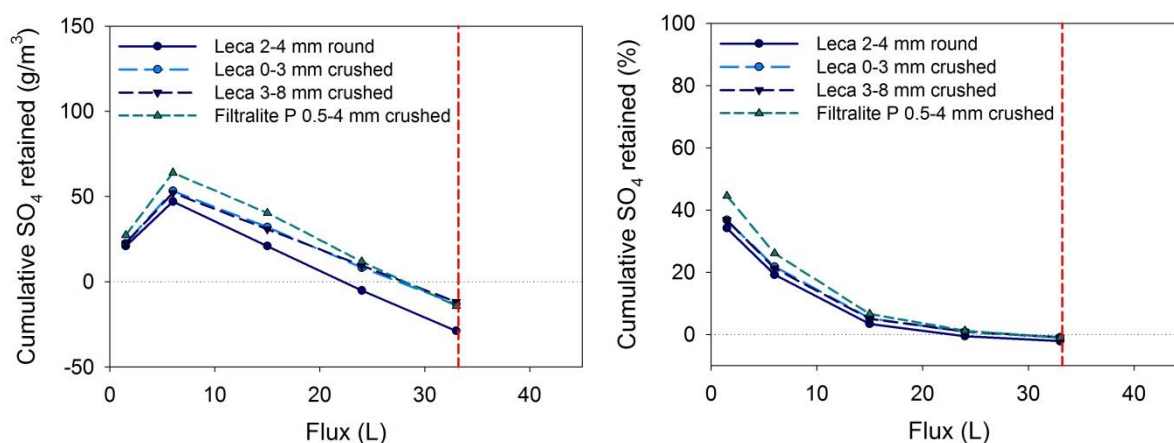


Figure 24. Cumulative sulfate ( $\text{SO}_4^{2-}$ ) retention or release by Leca and Filtralite® products in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

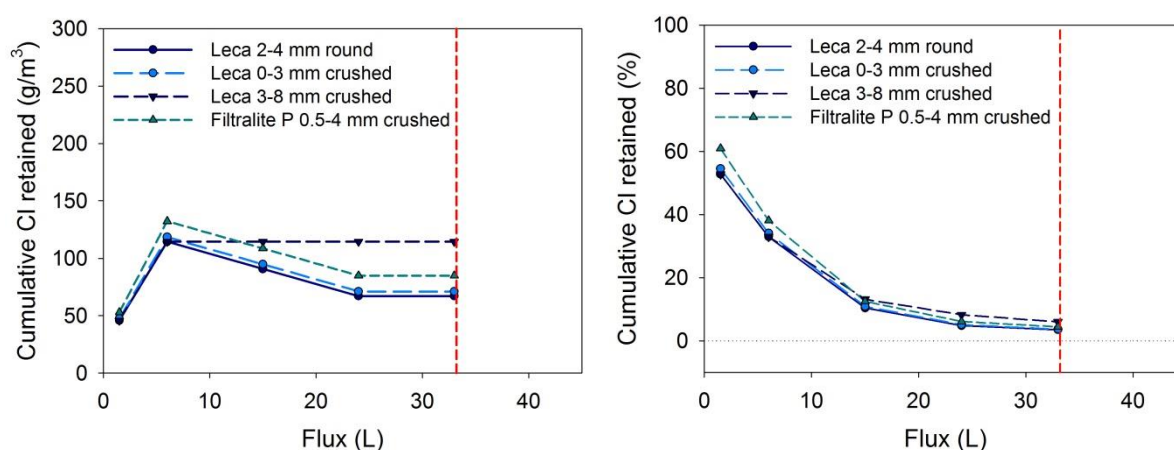


Figure 25. Cumulative chloride ( $\text{Cl}^-$ ) retention by Leca and Filtralite® products in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

Copper (Figure 26), lead (Figure 27) and zinc (Figure 28) were all effectively removed from influent stormwater and retained by all Leca and Filtralite® products. The Leca 3–8 mm crushed material exhibited slightly lesser attenuation of copper, lead and zinc relative to other Leca and Filtralite® products. The observed difference in metal sorption between the Leca 3–8 mm crushed product and others is most likely a function of the relative bulk densities of the packed materials. Each of the Leca and Filtralite® products possesses a similar internal surface area (ca.  $1\,000\,000\,\text{m}^2/\text{m}^3$ ) and bulk specific surface area of  $0.25\text{--}1.0\,\text{m}^2/\text{g}$  (J. Wood, personal communication). Differences in the packed bulk density of each product, however, may result in the Leca and Filtralite® products exhibiting a substantially different specific surface area, and thus different volumetric density of metal sorption sites. Assuming equal bulk specific surface area among all Leca and Filtralite® products, differences in packed bulk density yield 50% lower specific surface area per  $\text{m}^3$  of Leca 3–8 mm crushed material compared with the Leca 2–4 mm round material. Thus, the lesser proportion of influent metals retained by the Leca 3–8 mm crushed material relative to other Leca and Filtralite® products is likely due to the substantially lesser bulk density of the packed Leca 3–8 mm filter material.

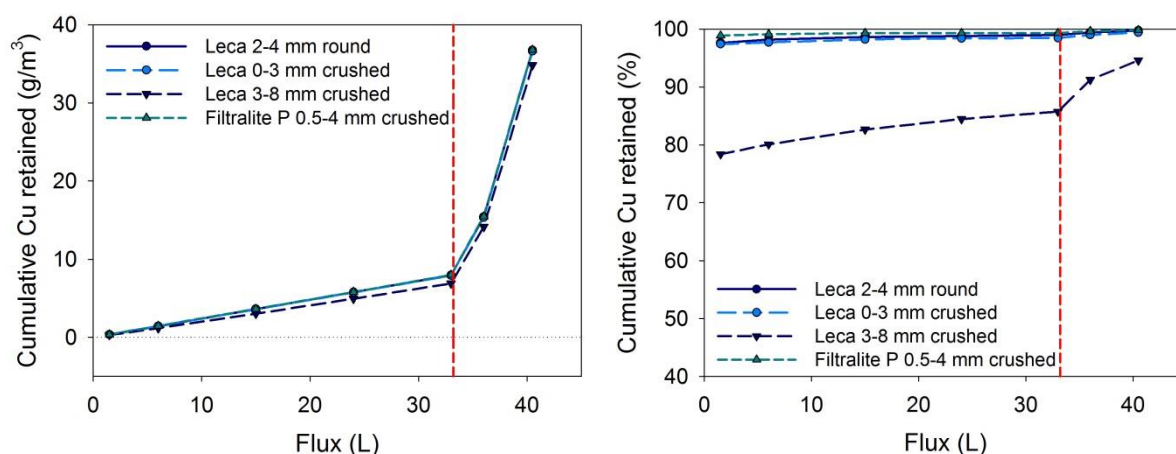


Figure 26. Cumulative copper (Cu) retention by Leca and Filtralite® products in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

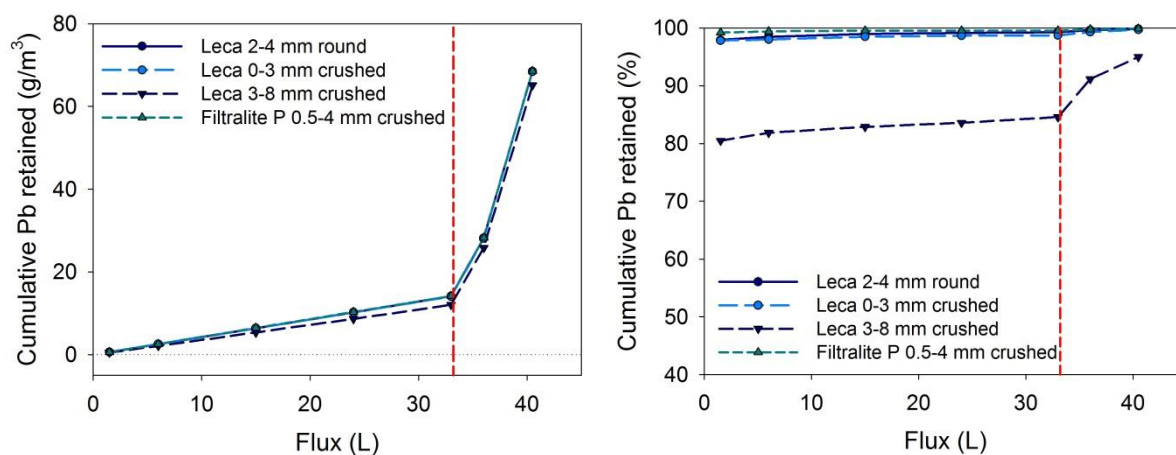


Figure 27. Cumulative lead (Pb) retention by Leca and Filtralite® products in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

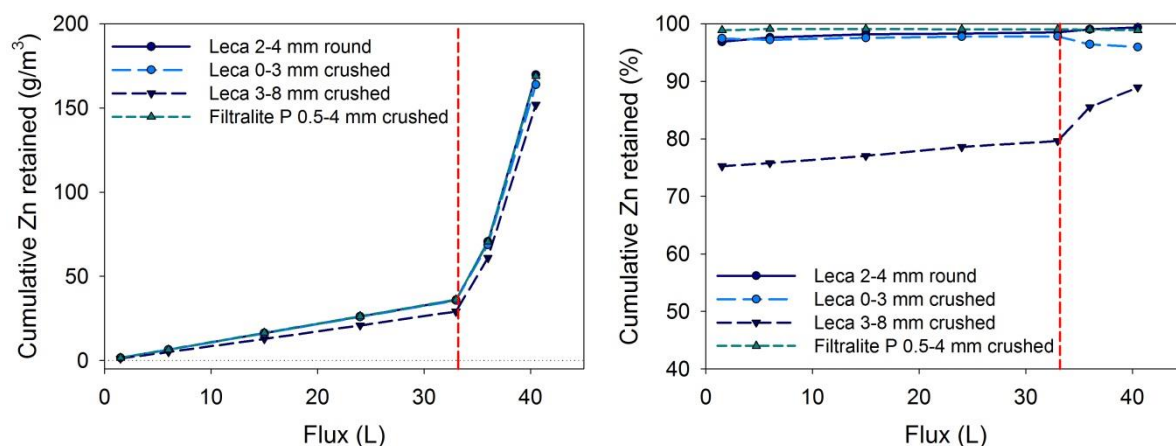


Figure 28. Cumulative zinc (Zn) retention by Leca and Filtralite® products in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

The phosphorus concentration in the effluents from columns the Leca and Filtralite® products, with the exception of Leca 3–8 mm crushed material, was less than analytical detection limits (50 µg/L) when influent stormwater phosphorus concentration was 500 µg/L (i.e., 0–33 L). After the addition of a further 7.5 L of twenty-fold concentrated stormwater with nominal P concentration 1 mg/L the cumulative retention of added phosphorus by all Leca and Filtralite® products was ≥90% (Figure 29).

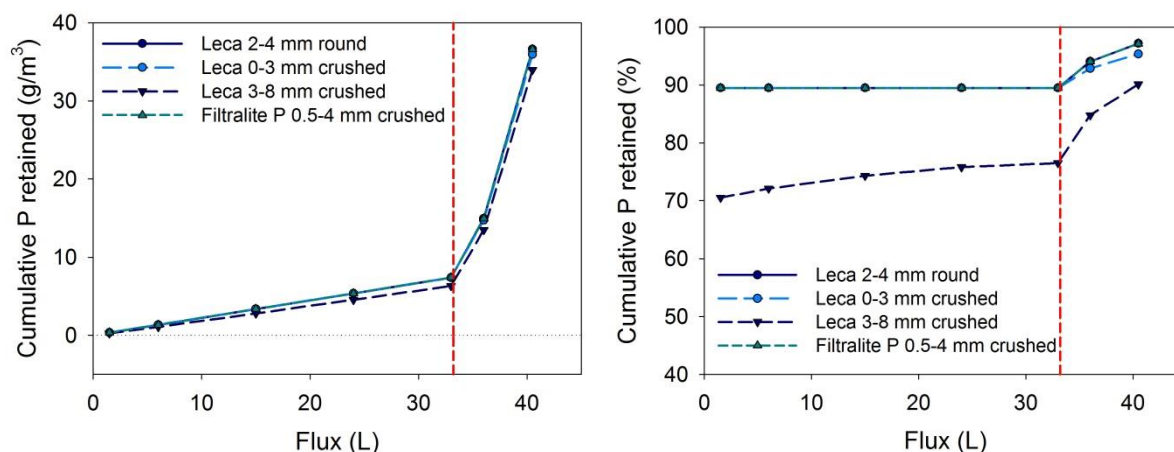


Figure 29. Cumulative phosphorus (P) retention by Leca and Filtralite® products in flow-through column testing, expressed in mg/kg (left), g/m³ (middle), and as per cent of total (right).

### 5.1.3 Peat filter materials

Despite the acid pH of 1:5 solid to liquid extracts of both peat and peat + 10 wt.% limestone (Table 2), effluents from the columns containing peat and peat + 10 wt.% limestone remained between pH ca. 6.5 and 7 (Figure 30). The observed increase in effluent from the peat + 10 wt.% limestone column when influent pH decreased to 6.25 is indicative of limestone dissolution as the ambient solution pH decreased.

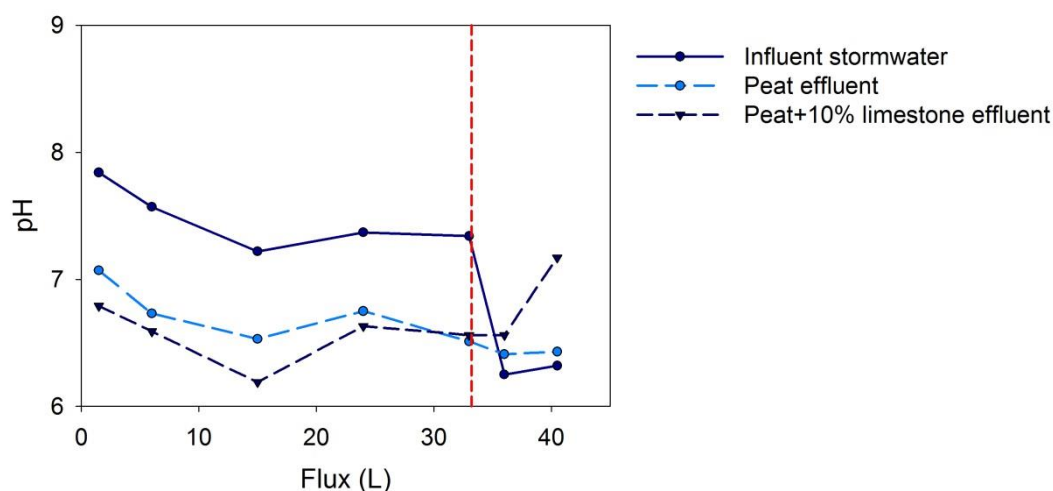


Figure 30. Influent stormwater pH and pH of effluents from columns containing peat filter materials.

As observed previously for aggregate and light expanded clay aggregate filter materials, both peat and peat + 10 wt.% limestone initially retained some of the sulfate (Figure 31) and



chloride (Figure 32) in influent synthetic stormwater. The anions initially sorbed to peat products were gradually flushed from the materials with further addition of stormwater to experimental columns, resulting in no net retention of sulfate and limited chloride retention.

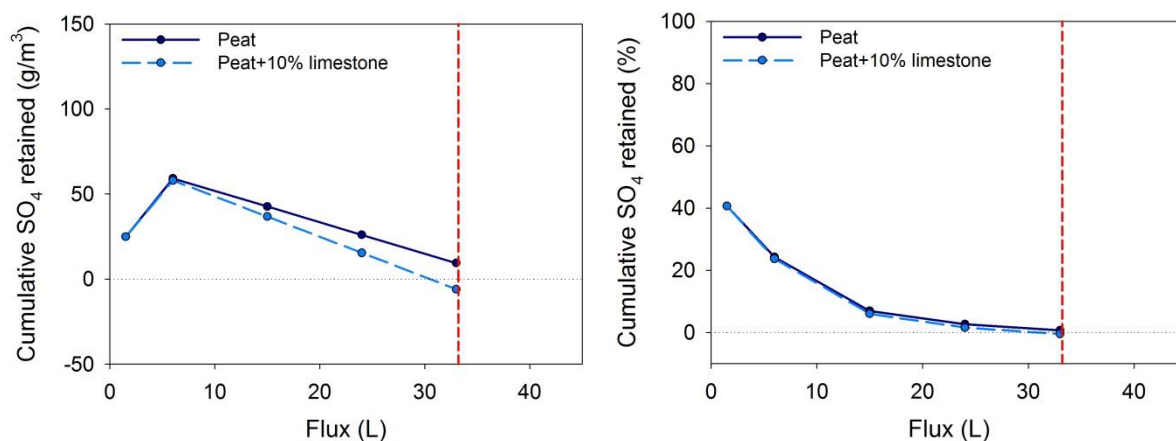


Figure 31. Cumulative sulfate ( $\text{SO}_4^{2-}$ ) retention or release by peat filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

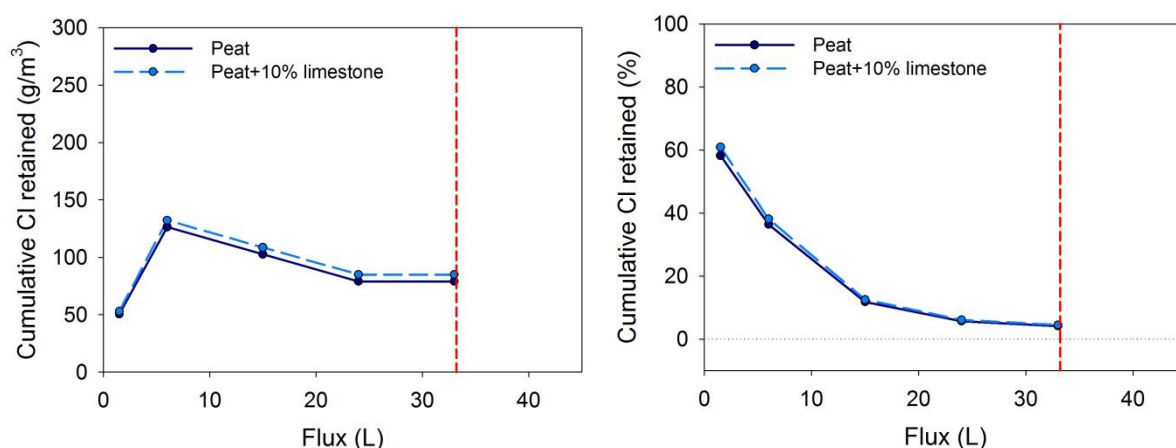


Figure 32. Cumulative chloride ( $\text{Cl}^-$ ) retention by peat filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

The peat + 10 wt.% limestone mixture retained a greater proportion of copper (Figure 33), lead (Figure 34), and zinc (Figure 35) from influent synthetic stormwater compared with only peat. This difference is likely due to the presence of limestone ( $\text{CaCO}_3$ ) in the peat-limestone mixture<sup>25</sup>. The lignin, cellulose and humic acid constituents of peat have surface functional groups including carboxylic acids, phenolic hydroxides, ethers, alcohols, aldehydes, and ketones which can be involved in chemical reactions<sup>27</sup>. Peat has been shown to retain metals in the order  $\text{Pb} > \text{Cu} > \text{Ni} > \text{Cd} > \text{Zn}$  in adsorption isotherm experiments<sup>28</sup>. In the present study, metals were retained in the order  $\text{Zn} > \text{Pb} > \text{Cu}$ , consistent with each metal's respective concentration in influent solution (see Table 5) and with previous work showing increased metal uptake by peat with increasing solution pH<sup>27</sup>. Due to its polar character, peat possesses a high specific adsorption potential for metals and polar organic molecules<sup>29</sup>.

<sup>27</sup> Chaney, R.L., Hundemann, P.T. 1979. *Journal of the Water Pollution Control Federation* 51:17-21.

<sup>28</sup> Kalmykova, Y., Strömwell, A.-M., Steenari, B.-M. 2008. *Journal of Hazardous Materials* 152:885-891.

<sup>29</sup> Brown, P.A., Gill, S.A., Allen, S.J. 2000. *Water Research* 34:3907-3916.



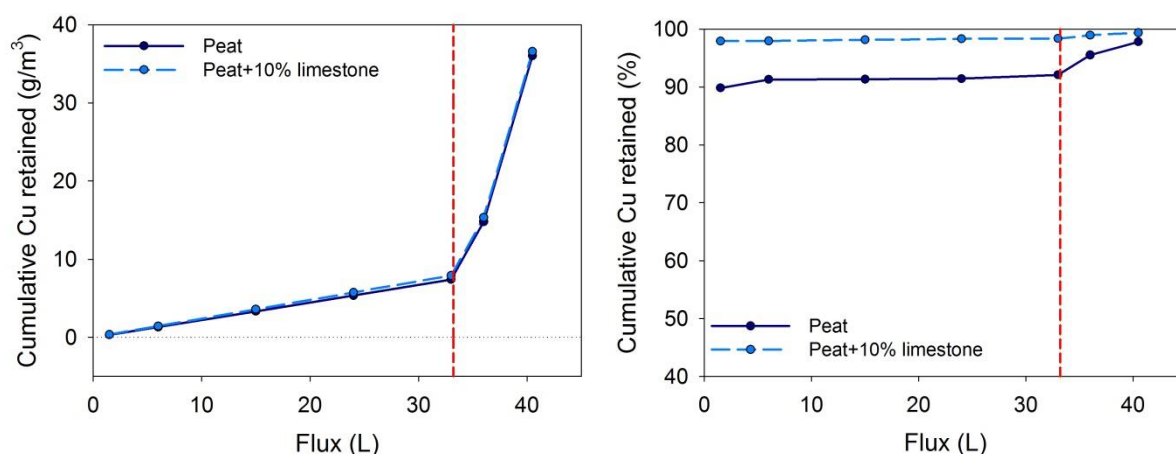


Figure 33. Cumulative copper (Cu) retention by peat filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

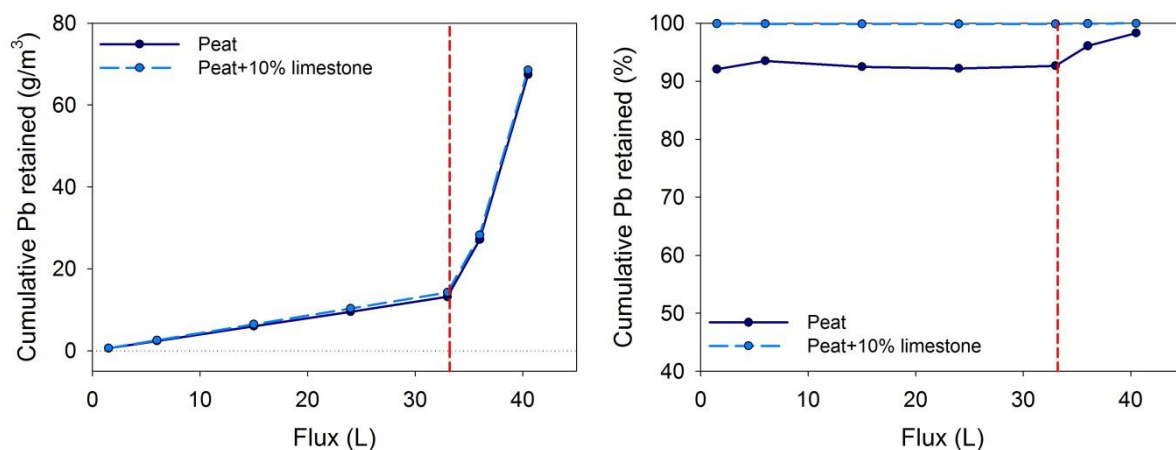


Figure 34. Cumulative lead (Pb) retention by peat filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

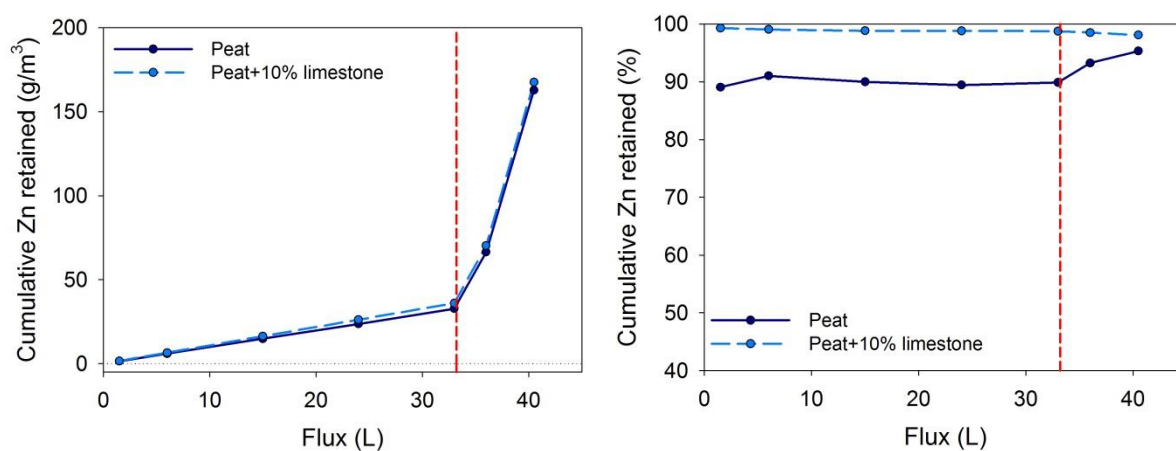


Figure 35. Cumulative zinc (Zn) retention by peat filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

The phosphorus sorption capacity of peat has been shown to be strongly correlated with the Fe and/or Al content of the peat<sup>30,31</sup>. The Fe and Al content of the peat products used in the present study was not determined; however, phosphorus attenuation by the peat products (Figure 36) was comparable to both the aggregate filter and materials and the Leca and Filtralite<sup>®</sup> products. Similar to metal retention, phosphorus retention by the peat + 10 wt.% limestone product was superior to peat alone. Phosphorus is known to rapidly sorb to CaCO<sub>3</sub> surfaces in soils, and, at high solution concentration to form calcium phosphate mineral precipitates<sup>32</sup>. Given the low concentration of phosphorus in the synthetic stormwater used herein, the mechanism of enhanced phosphorus attenuation by the peat + 10 wt.% limestone mixture was most likely due to sorption of phosphate (PO<sub>4</sub><sup>3-</sup>) from solution to the surface of limestone particles.

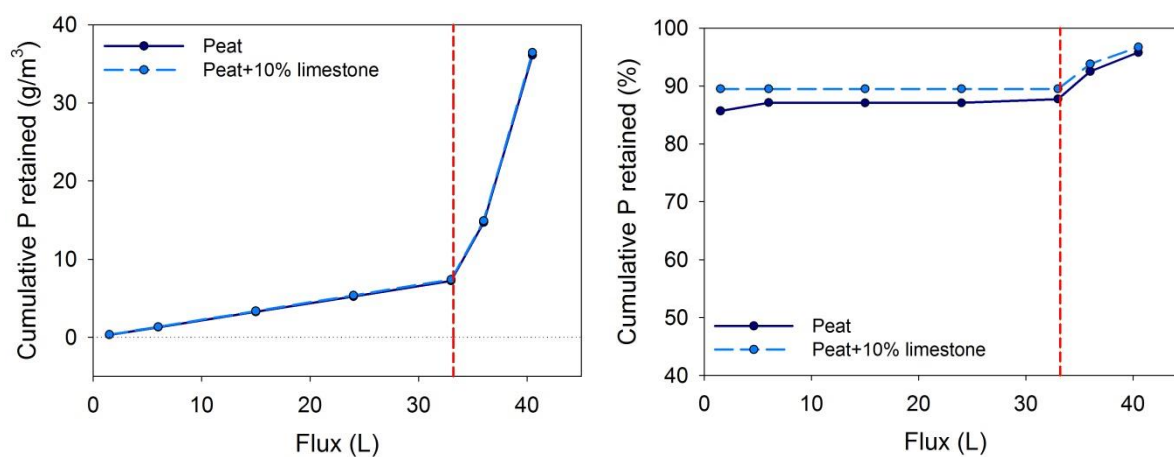


Figure 36. Cumulative phosphorus (P) retention by peat filter materials in flow-through column testing, expressed in g/m<sup>3</sup> (left) and as per cent of total (right).

#### 5.1.4 Biochar filter materials

Both the birch and spruce biochar column effluents were slightly to moderately alkaline but within the pH 6.5–8.5 range of freshwaters with healthy, diverse and productive fish and macroinvertebrate communities<sup>33</sup>.

<sup>30</sup> Nieminen, M., Jarva, M. 1996. *Scandinavian Journal of Forest Research* 11:321-326.

<sup>31</sup> Richardson, C.J. 1985. *Science* 228(4706):1424-1427.

<sup>32</sup> Cole, C.V., Sterling, R.O., Scott, C.O. 1953. *Soil Science Society of America Journal* 17:352-356.

<sup>33</sup> Robertson.Bryan, Inc. 2004. *pH Requirements of Freshwater Aquatic Life*.

[http://www.swrcb.ca.gov/rwqcb5/water\\_issues/basin\\_plans/ph\\_turbidity/ph\\_turbidity\\_04phreq.pdf](http://www.swrcb.ca.gov/rwqcb5/water_issues/basin_plans/ph_turbidity/ph_turbidity_04phreq.pdf)

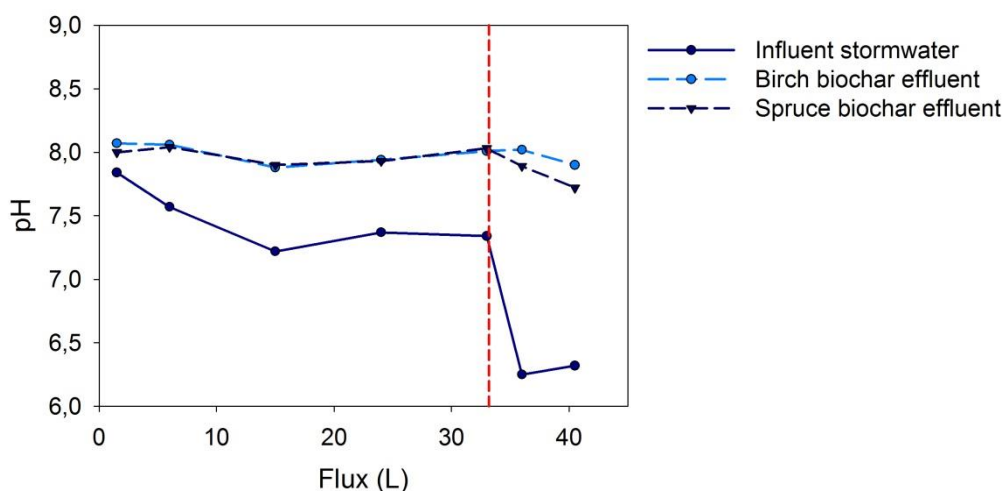


Figure 37. Influent stormwater pH and pH of effluents from columns containing biochar filter materials.

The birch and spruce biochars initially retained some of the sulfate (Figure 38) and chloride (Figure 39) in influent synthetic stormwater. The sulfate and chloride initially sorbed to birch or spruce biochar were gradually flushed from the materials with further addition of stormwater to experimental columns, resulting in no net retention of sulfate and limited chloride retention. Results showed a small net increase in cumulative solution sulfate in effluents from the birch biochar column, indicating that the birch biochar leached a small quantity of sulfate. The birch and spruce biochars both retained a small proportion of influent chloride after filtration of 30 L of synthetic stormwater.

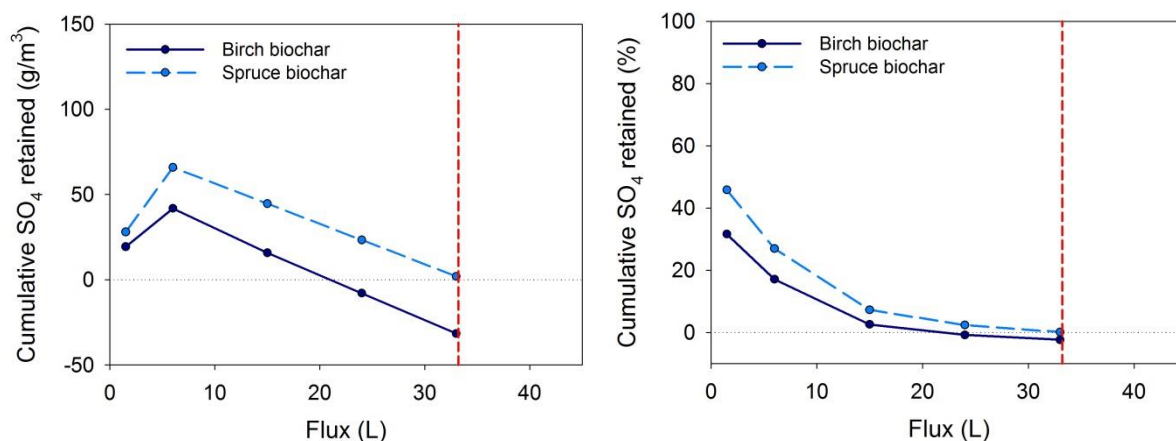


Figure 38. Cumulative sulfate ( $\text{SO}_4^{2-}$ ) retention or release by biochar filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

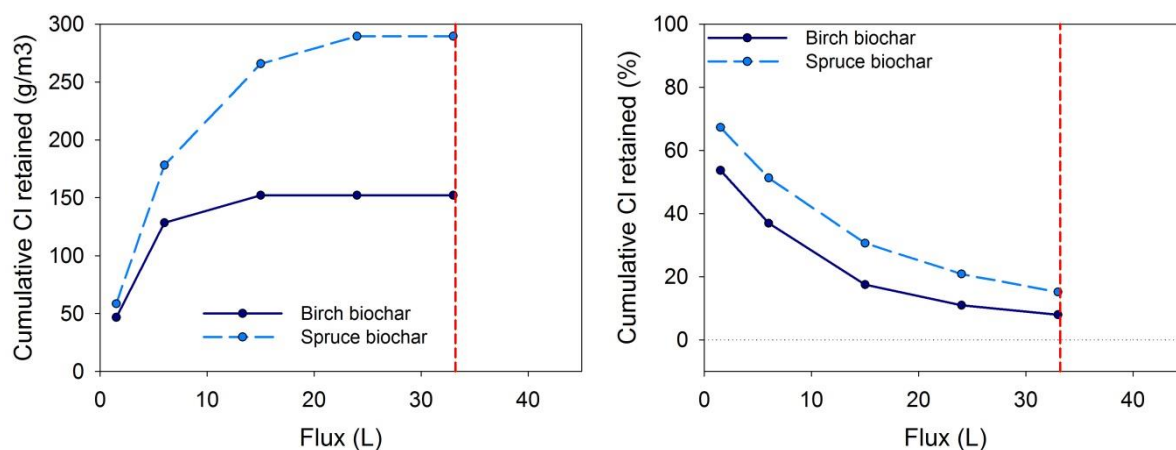


Figure 39. Cumulative chloride (Cl) retention by biochar filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

Compared with the birch biochar, the spruce biochar exhibited superior retention of copper (Figure 40), lead (Figure 41) and zinc (Figure 42) from influent synthetic stormwater.

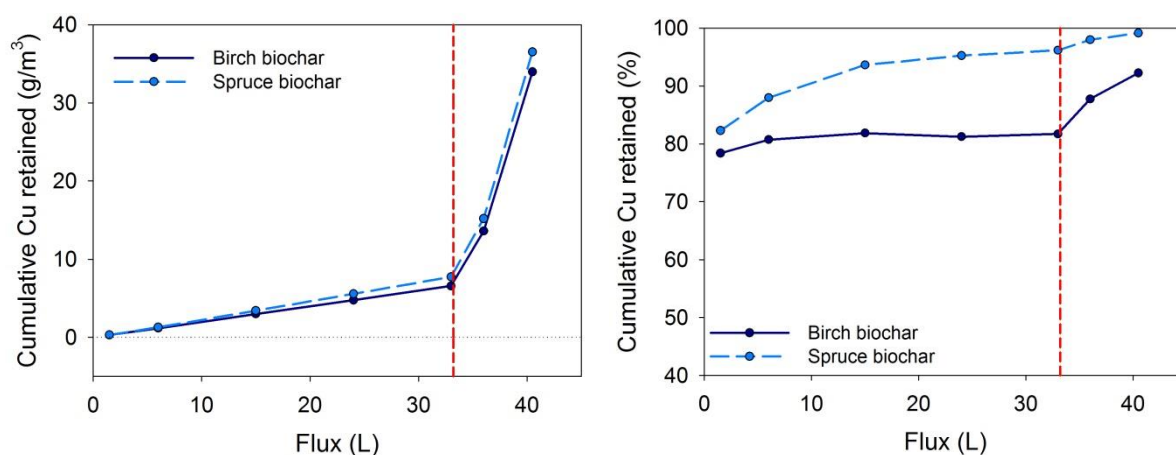


Figure 40. Cumulative copper (Cu) retention by biochar filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

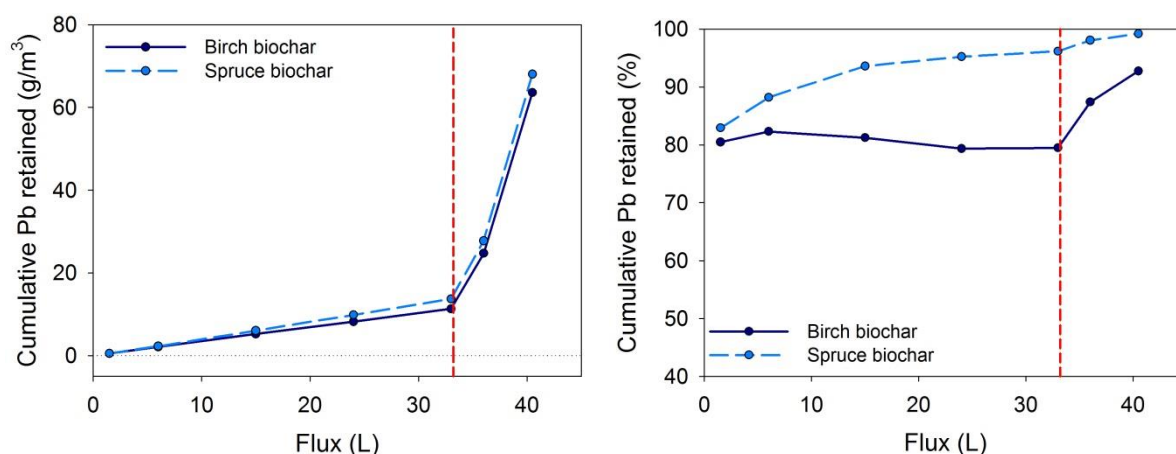


Figure 41. Cumulative lead (Pb) retention by biochar filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

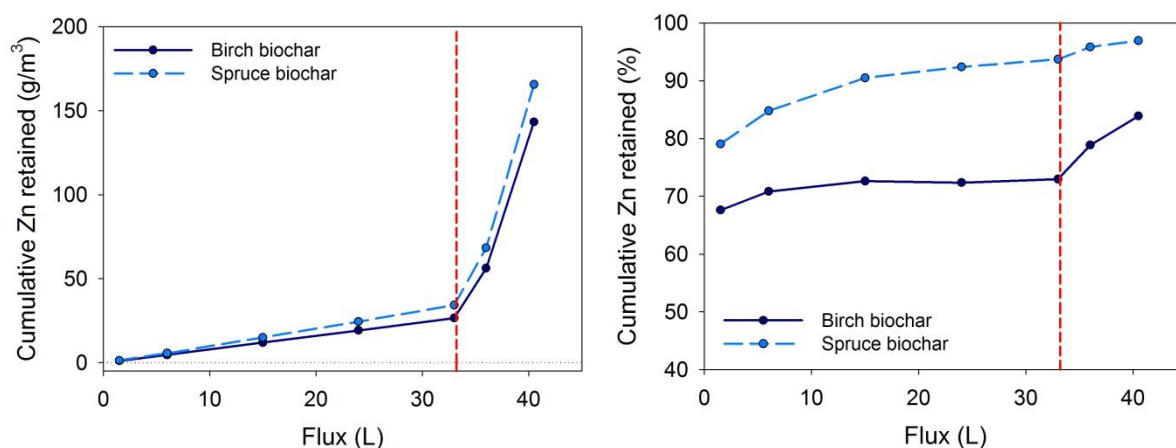


Figure 42. Cumulative zinc (Zn) retention by biochar filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

Phosphorus from influent synthetic stormwater was effectively retained by the spruce biochar (Figure 43). In contrast, effluents from the birch biochar column initially exhibited greater phosphorus concentration than the influent stormwater, indicating that the birch biochar initially leached phosphorus from the solid material.

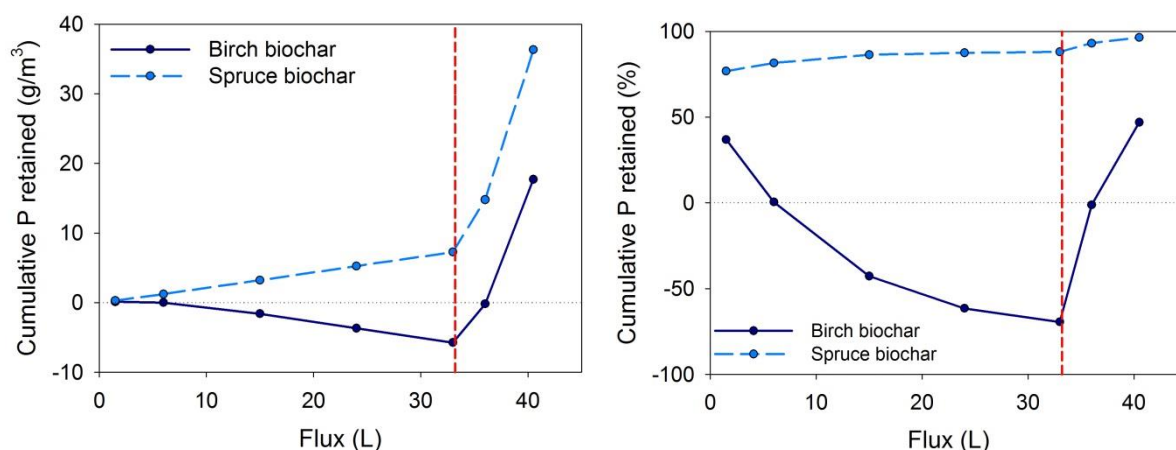


Figure 43. Cumulative phosphorus (P) retention by biochar filter materials in flow-through column testing, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

## 5.2 Column Trials Using 10X Concentrated Synthetic Stormwater

The initial column trials demonstrated that each material had an approximately equal pollutant attenuation capacity in the near- to mid-term (e.g.  $\leq 3$  years) under the given conditions of a realistic first-flush stormwater. Based on the initial column trial results it was not possible to determine the sorption capacity and thus the potential lifetime of individual filter materials. Nor was it possible to identify materials likely to exhibit synergies with respect to the removal of pollutants from stormwater, and thus potentially suitable for use in layered systems. Additional column experiments were conducted in an attempt to load individual materials to excess with metals (copper, lead, and zinc) and phosphorus in the absence of potential interferences. Organic carbon was added to the original synthetic stormwater to simulate a typical organic carbon concentration reported in field-based stormwater investigations. Organic carbon is a natural buffer and has the potential to interfere with metal and/or phosphorus sorption to solid surfaces.

Due to the inherent variability in stormwater composition, as well as the lack of differentiation among materials or observed contaminant breakthrough in initial columns experiments, additional column experiments were conducted using individual materials. The same column configuration was used in both the initial and continuing column experiments (Figure 8). The synthetic stormwater composition differed in that it was more concentrated than that used in the initial experiments, and contained no organic carbon. This represents a 'worst-case' scenario for stormwater runoff, wherein there are no potential buffers to pollutant solubility. Metals (copper, lead, zinc) and phosphorus were present in the synthetic stormwater used for the second set of column trials at 10X the original concentration, as shown in Table 6.



Table 6. StormFilter project nominal synthetic stormwater composition for laboratory column testing.

	Initial trial, 0–33 liters	Initial trial, 33–40.5 liters	Second column trial
	1X Nominal Concentration (µg/L)	20X Nominal Concentration (µg/L)	10X Nominal Concentration (µg/L)
<b>Cu</b>	500	10 000	5 000
<b>Pb</b>	1 000	20 000	10 000
<b>Zn</b>	2 000	40 000	20 000
<b>Total P</b>	500	10 000	5 000
<b>Cl</b>	100 000	140 000	-
<b>SO<sub>4</sub></b>	80 000	94 000	-
<b>Organic carbon</b>	10 000	10 000	-

The intention of using 10X concentrated stormwater in the second set of column trials was to accelerate stormwater treatment simulation by individual materials in order to allow estimation of longer-term material performance during the term of the StormFilter project. The absence of organic carbon facilitates development of an understanding of metal partitioning between the solution and each solid phase in the absence of metal-organic carbon complex formation. This information may be extrapolated to evaluate how lead and copper concentrations may change with time or as a result of environmental changes, specifically changes in the organic carbon content of influent water or stability of metal-organic carbon complexes.

The second set of column containing individual filter materials were operated as previously described, with addition of 1.5 L aliquots of stormwater no more than once per 24-h period with periodic sampling to assess metal and phosphorus removal by each material. Results for the Leca 3–8 mm crushed material with 10X concentrated influent synthetic stormwater are not shown due to an issue with the column packing which resulted in unreliable concentration data.

The following figures show overall copper, zinc, lead and phosphorus retention by each material after filtration of 30 L of nominally 10X concentrated synthetic stormwater solution through each column. Most of the materials examined showed effective removal of copper (Figure 44), lead (Figure 45) and zinc (Figure 46) from the 10X concentrated synthetic stormwater solution. In comparison to the first column experiment using less concentrated synthetic stormwater, a greater proportion of copper, lead and zinc was retained from the ten-fold concentrated synthetic stormwater.

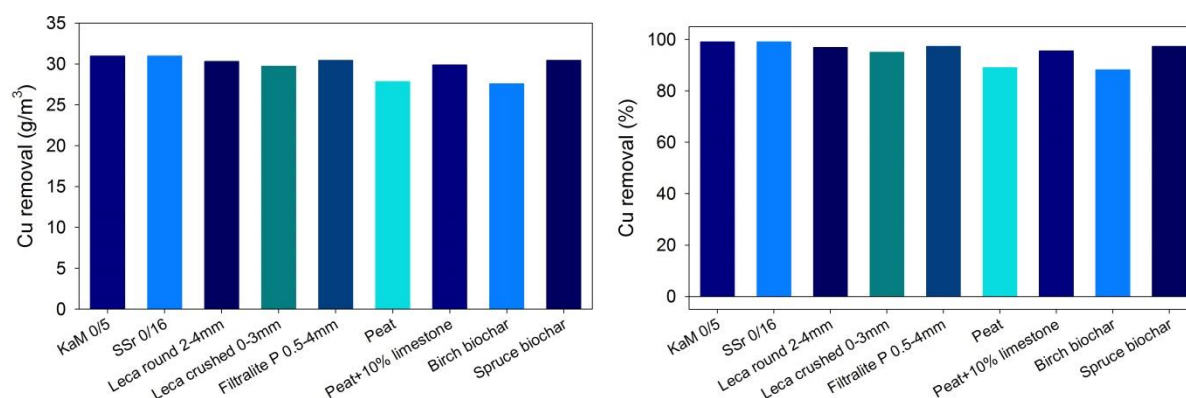


Figure 44. Overall copper (Cu) retention by selected materials in the second phase of column testing using 10X concentrated synthetic stormwater, expressed in g/m<sup>3</sup> (left) and as per cent of total (right).

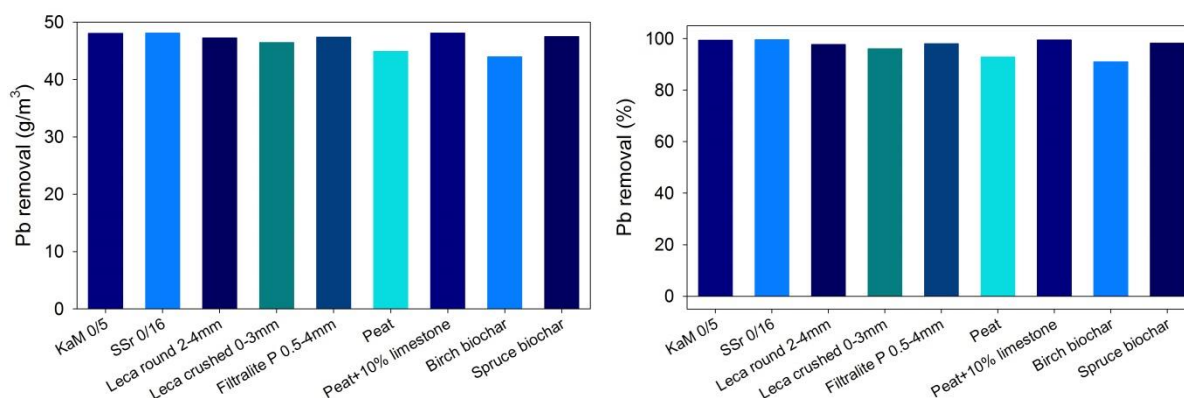


Figure 45. Overall lead (Pb) retention by selected materials in the second phase of column testing using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

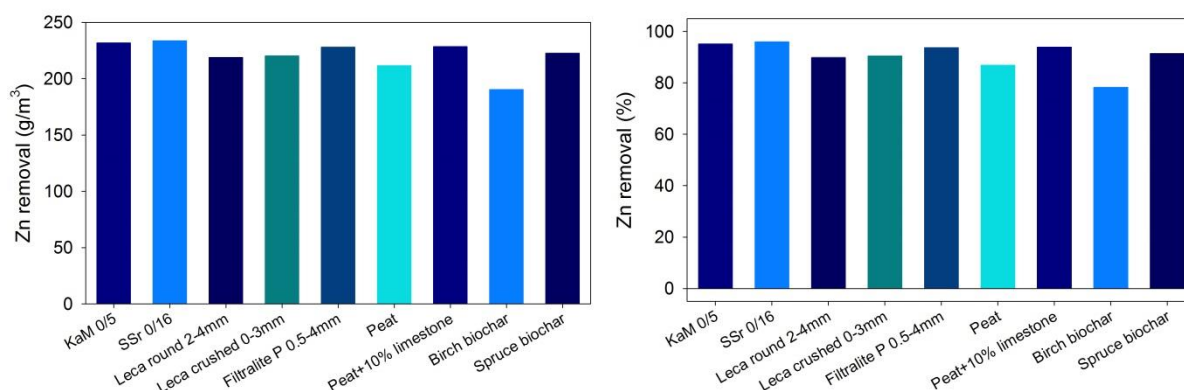


Figure 46. Overall zinc (Zn) retention by selected materials in the second phase of column testing using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

With the exception of the birch biochar, the filter materials examined showed effective removal of phosphorus (Figure 47). In contrast to the previous trial with lower concentration synthetic stormwater influent, the birch biochar did not exhibit an initial net increase in phosphorus concentration in column effluent relative to the influent stormwater; however, phosphorus retention by the birch biochar remained lesser in comparison to the spruce biochar.

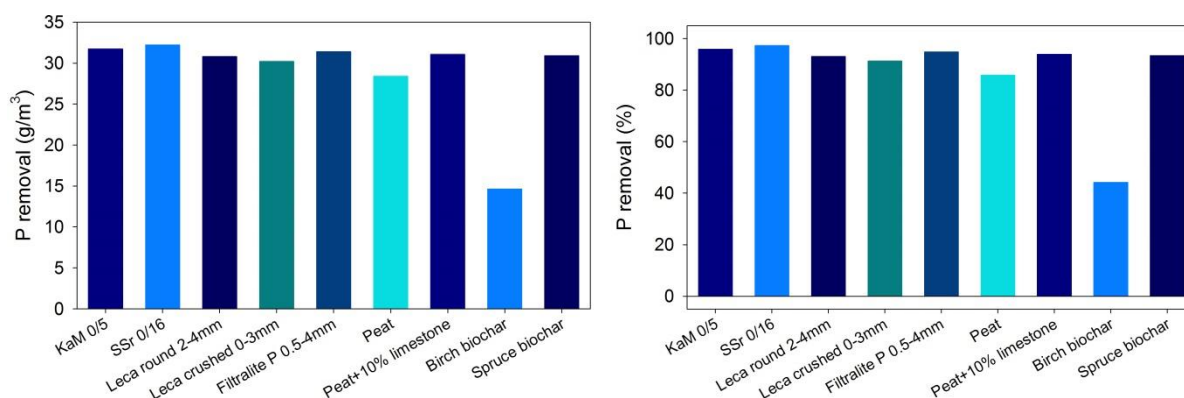


Figure 47. Overall phosphorus (P) retention by selected materials in the second phase of column testing using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

Detailed plots in the following sub-sections show stormwater influent and column effluent pH, and concentrations of analyzed elements Cu, Pb, Zn and P in each respective column effluent as a function of time (expressed as effluent flux) in the column experiment using 10X concentrated synthetic stormwater.

### 5.2.1 Aggregate filter materials

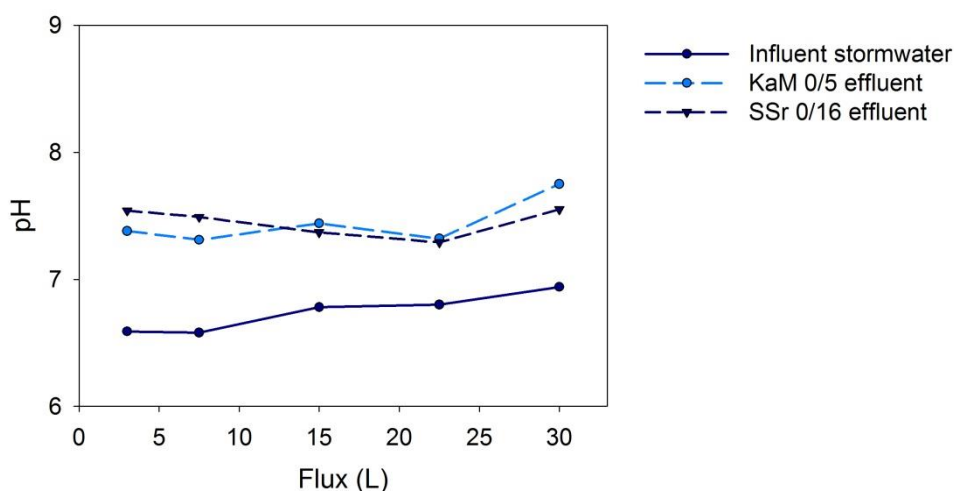


Figure 48. Influent 10X concentrated synthetic stormwater pH and the pH of effluents from columns containing aggregate filter materials.

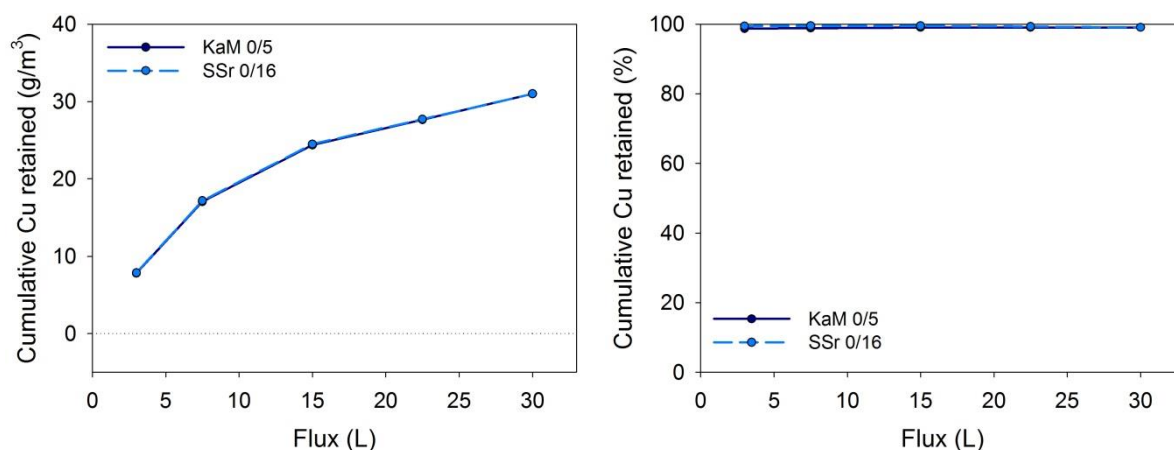


Figure 49. Cumulative copper (Cu) retention by aggregate materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

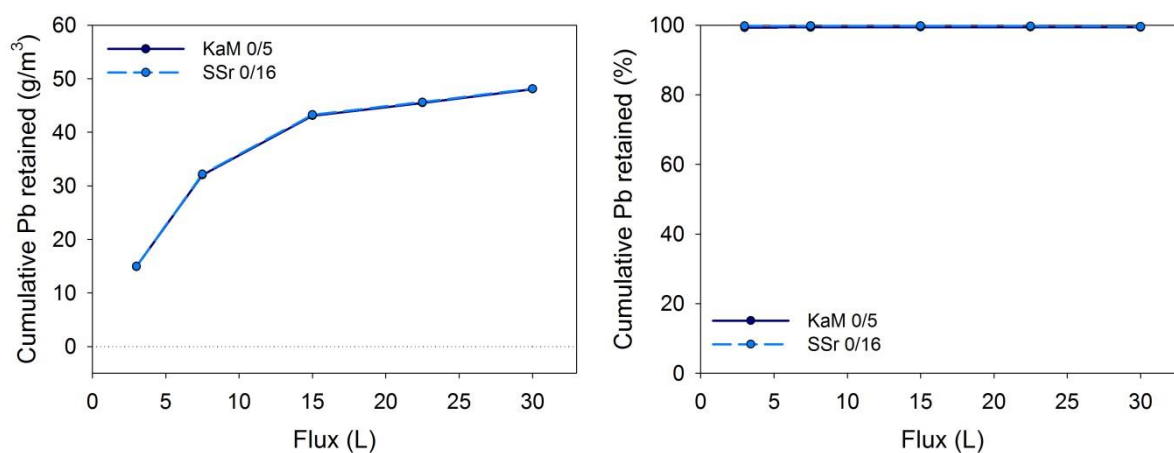


Figure 50. Cumulative lead (Pb) retention by aggregate materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

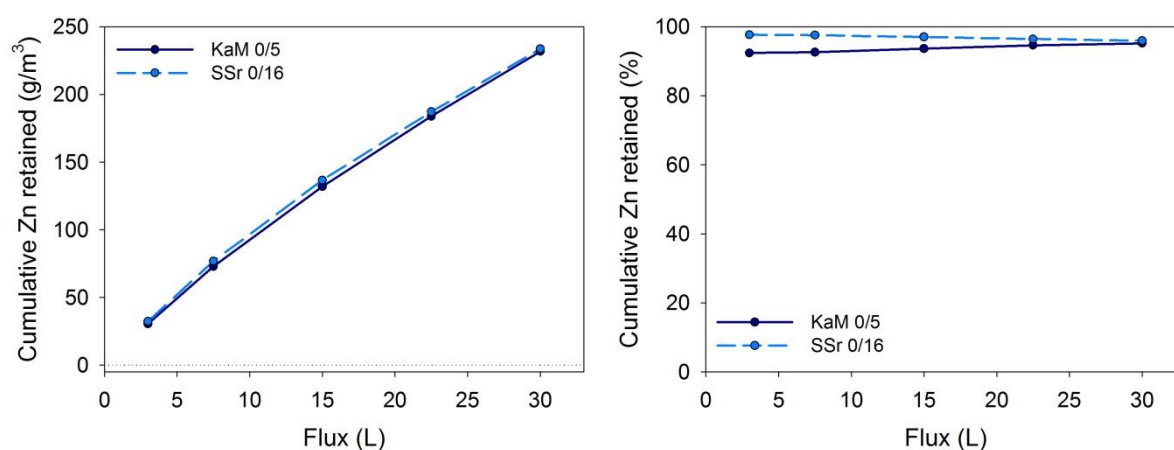


Figure 51. Cumulative zinc (Zn) retention by aggregate materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

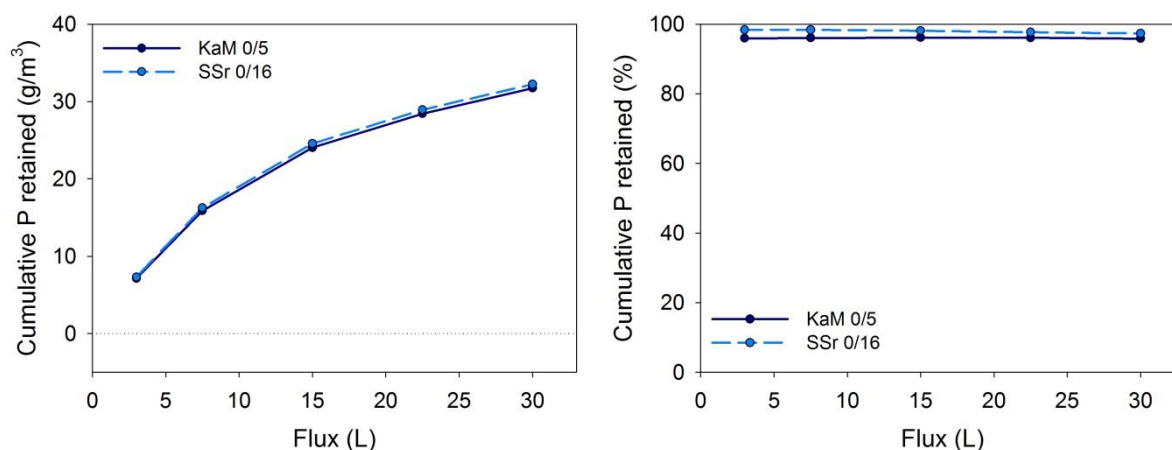


Figure 52. Cumulative phosphorus (P) retention by aggregate materials in column experiment using 10X concentrated synthetic stormwater, expressed in g/m<sup>3</sup> (left) and as per cent of total (right).

### 5.2.2 Leca and Filtralite® P filter materials

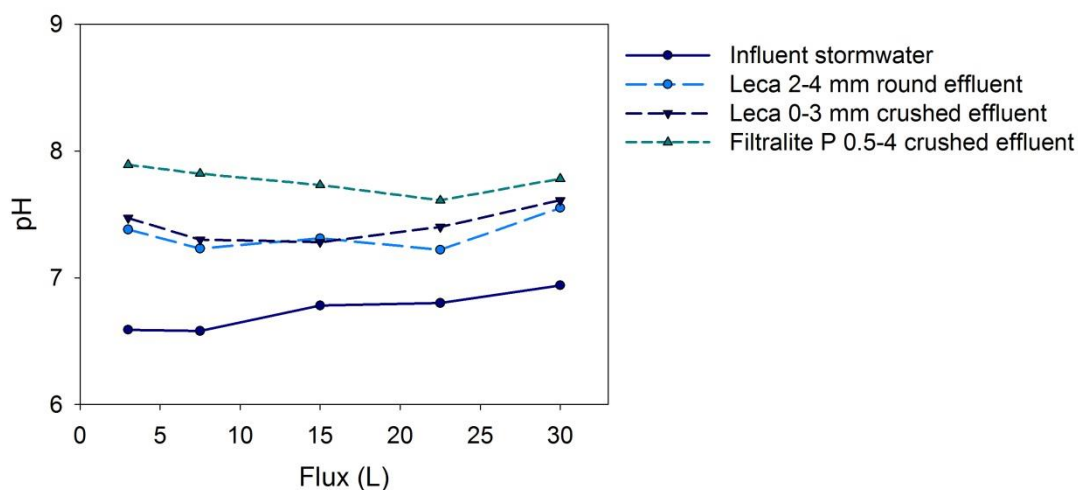


Figure 53. Influent 10X concentrated synthetic stormwater pH and the pH of effluents from columns containing Leca and Filtralite® products.

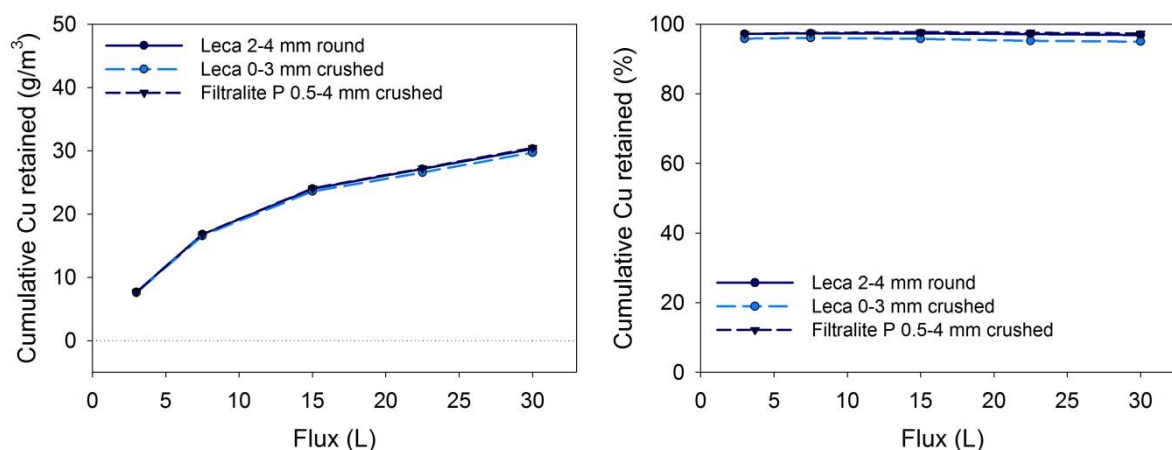


Figure 54. Cumulative copper (Cu) retention by Leca and Filtralite® products in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

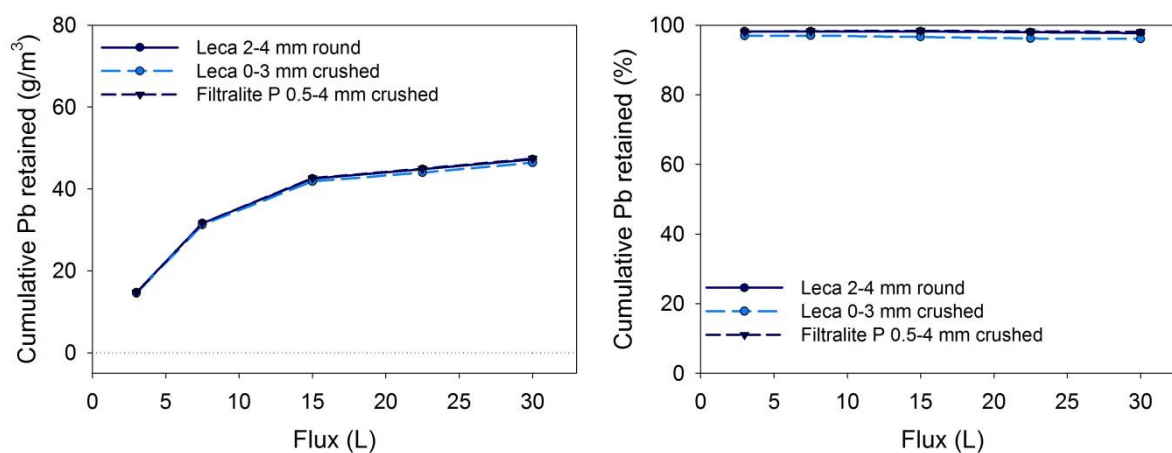


Figure 55. Cumulative lead (Pb) retention by Leca and Filtralite® products in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

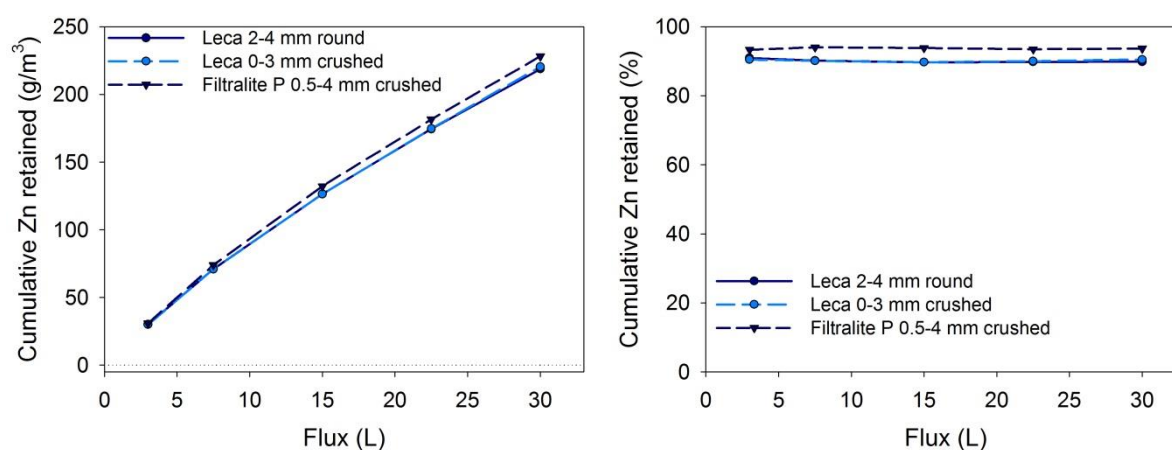
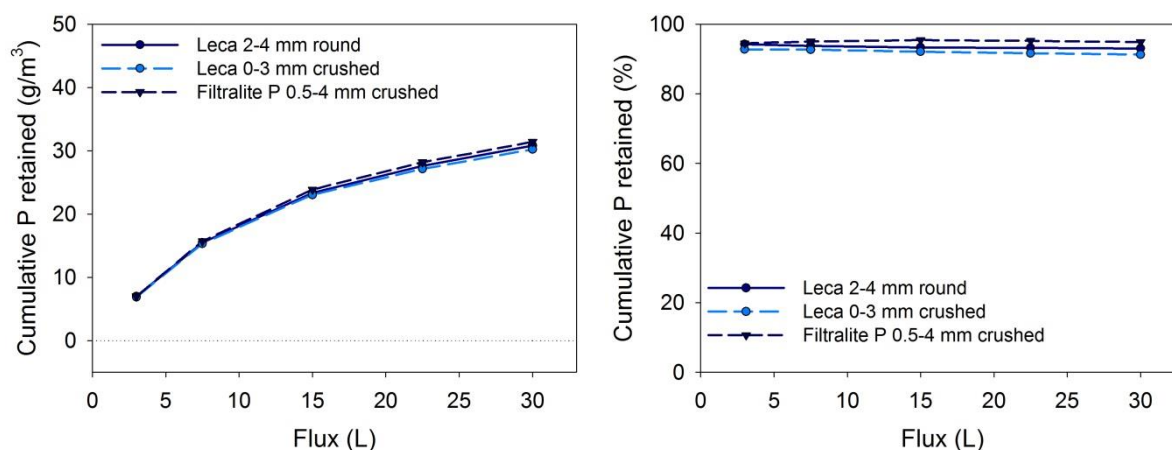


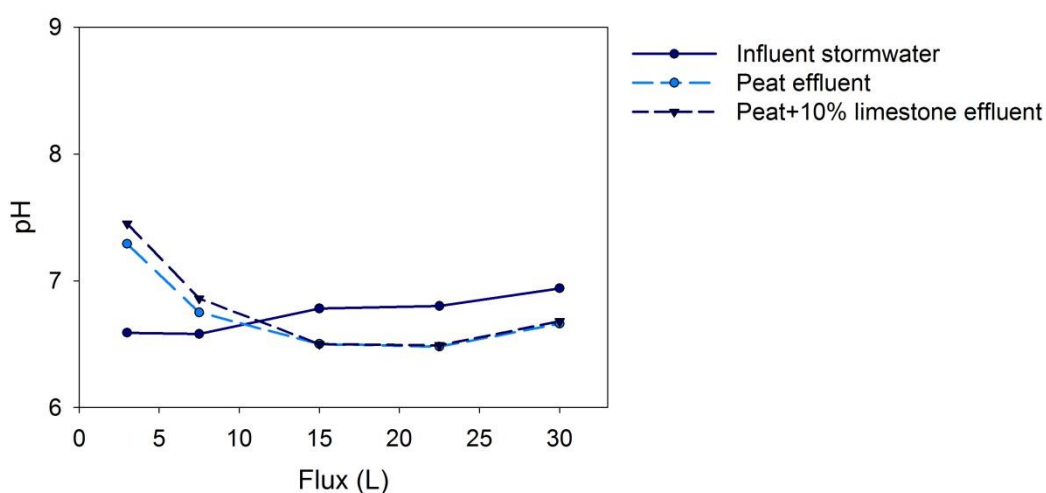
Figure 56. Cumulative zinc (Zn) retention by Leca and Filtralite® products in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).





**Figure 57.** Cumulative phosphorus (P) retention by Leca and Filtralite® products in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

### 5.2.3 Peat filter materials



**Figure 58.** Influent 10X concentrated synthetic stormwater pH and the pH of effluents from columns containing peat materials.

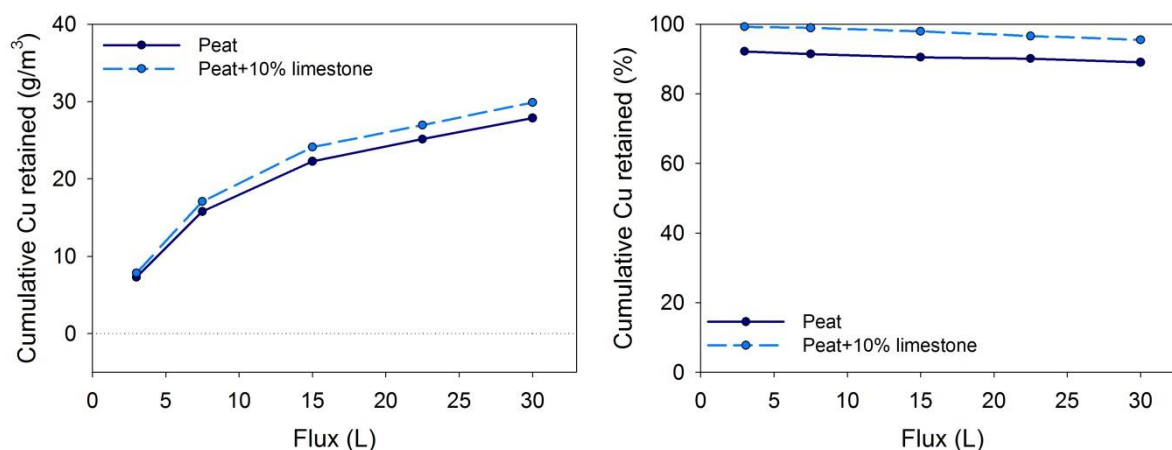


Figure 59. Cumulative copper (Cu) retention by peat materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

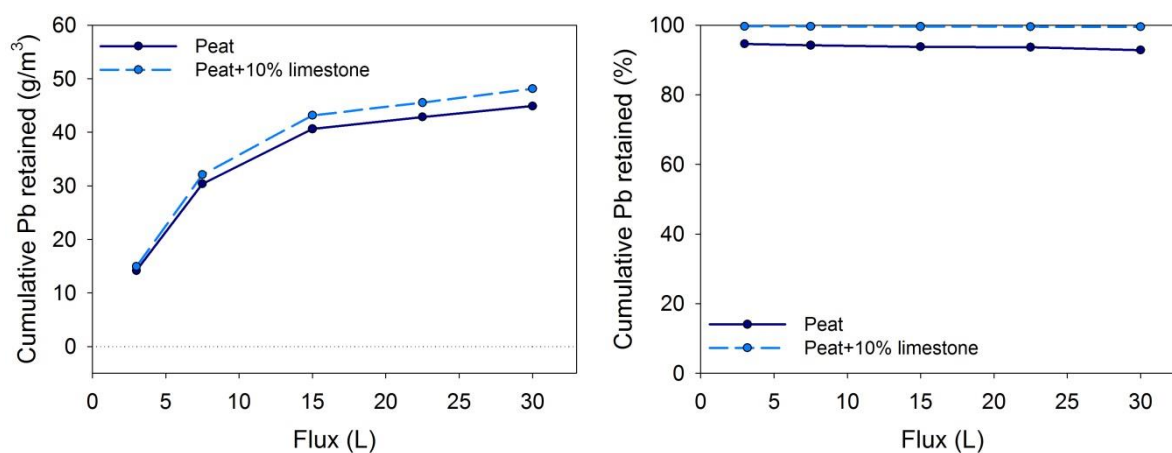


Figure 60. Cumulative lead (Pb) retention by peat materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

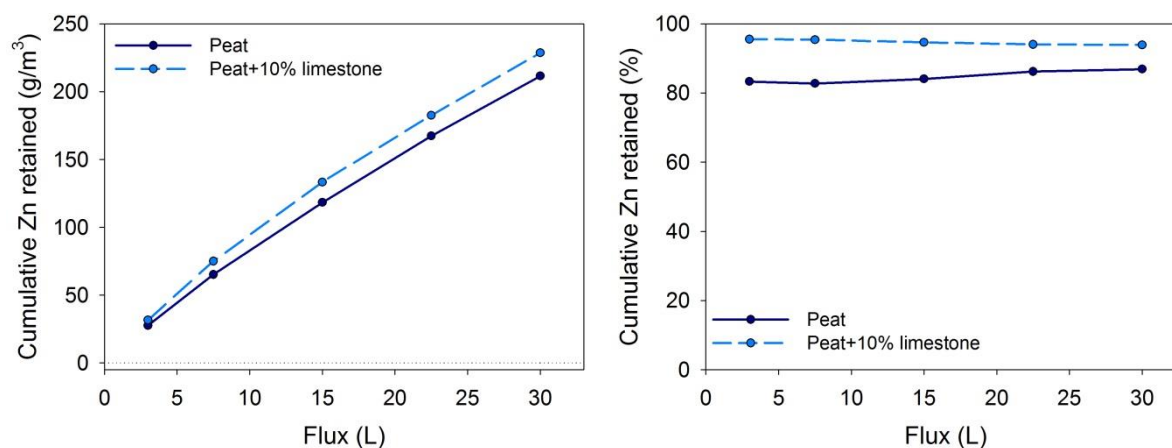


Figure 61. Cumulative zinc (Zn) retention by peat materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

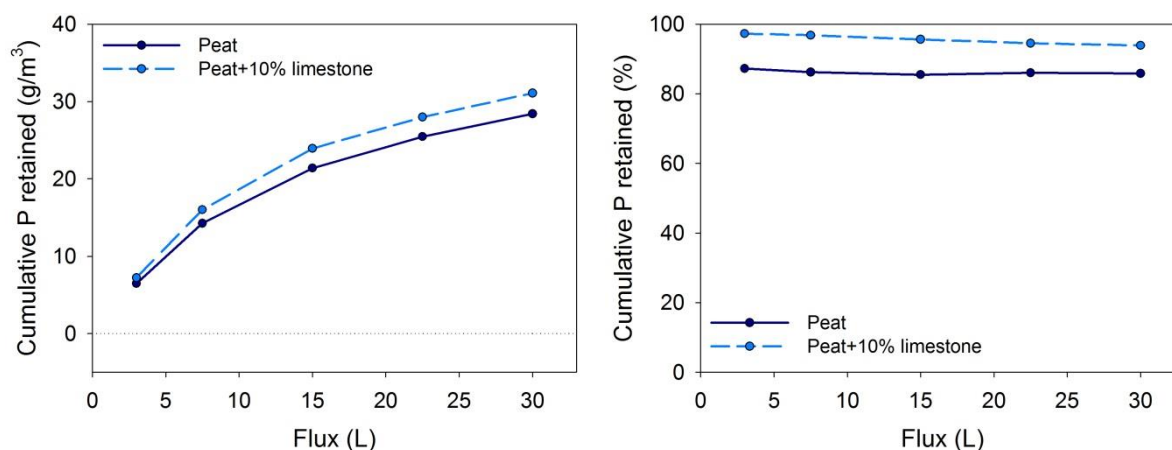


Figure 62. Cumulative phosphorus (P) retention by peat materials in column experiment using 10X concentrated synthetic stormwater, expressed in g/m<sup>3</sup> (left) and as per cent of total (right).

#### 5.2.4 Biochar filter materials

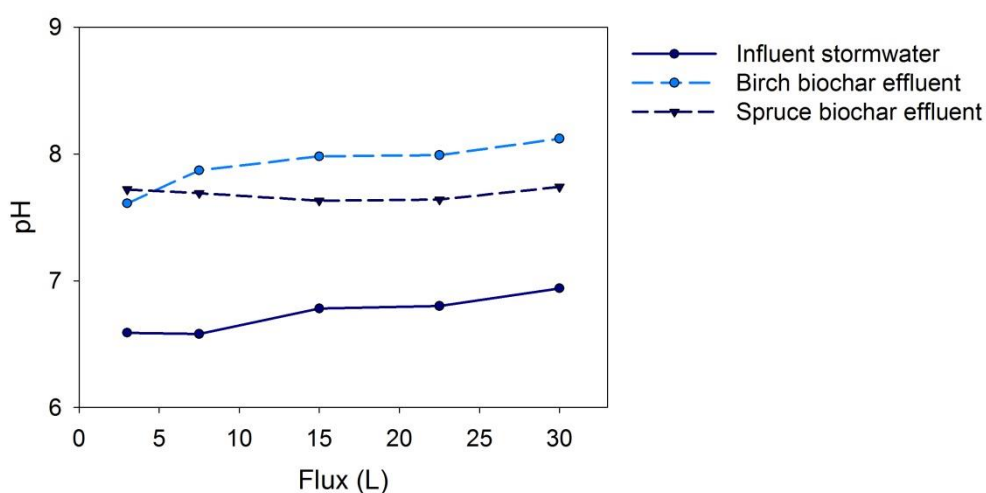


Figure 63. Influent 10X concentrated synthetic stormwater pH and the pH of effluents from columns containing biochar materials.

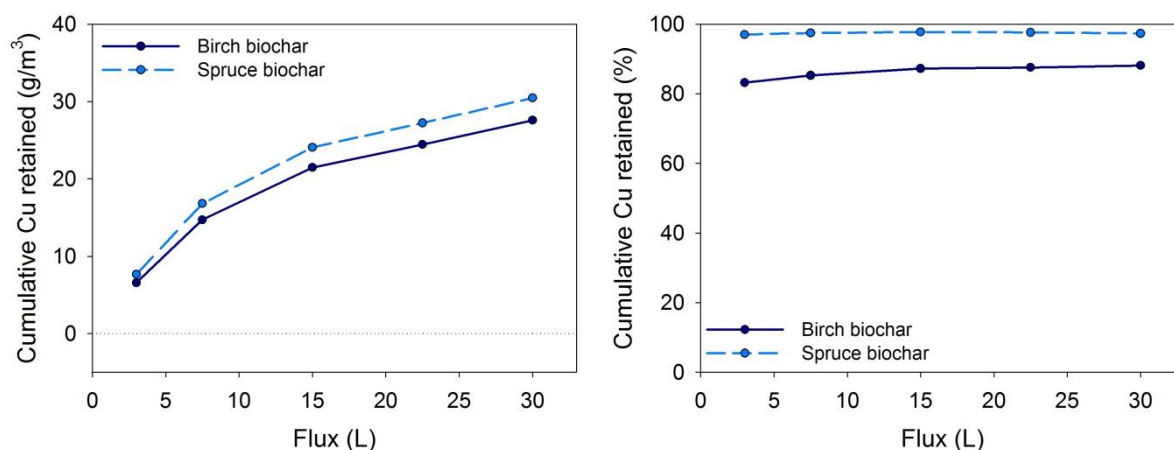


Figure 64. Cumulative copper (Cu) retention by biochar filter materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

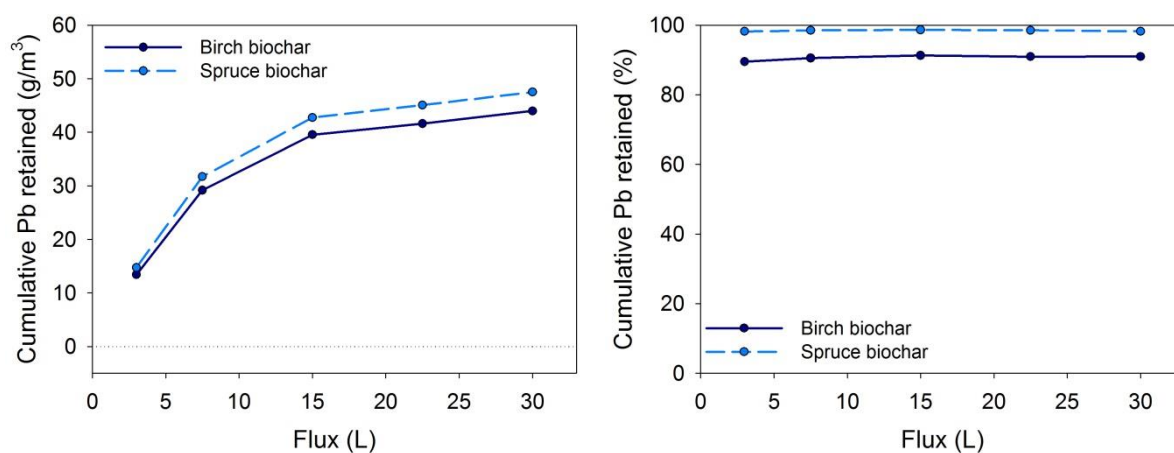


Figure 65. Cumulative lead (Pb) retention by biochar filter materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

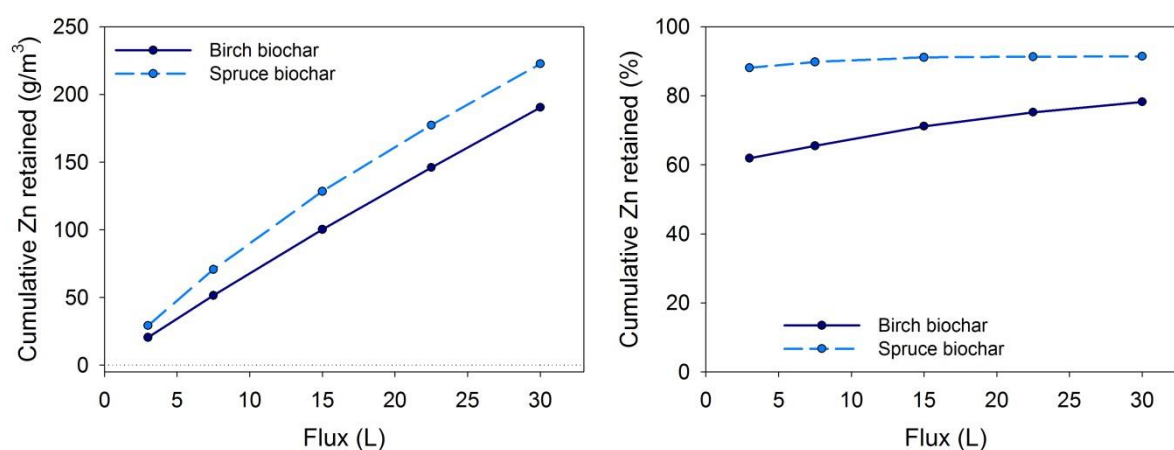


Figure 66. Cumulative zinc (Zn) retention by biochar filter materials in column experiment using 10X concentrated synthetic stormwater, expressed in  $\text{g/m}^3$  (left) and as per cent of total (right).

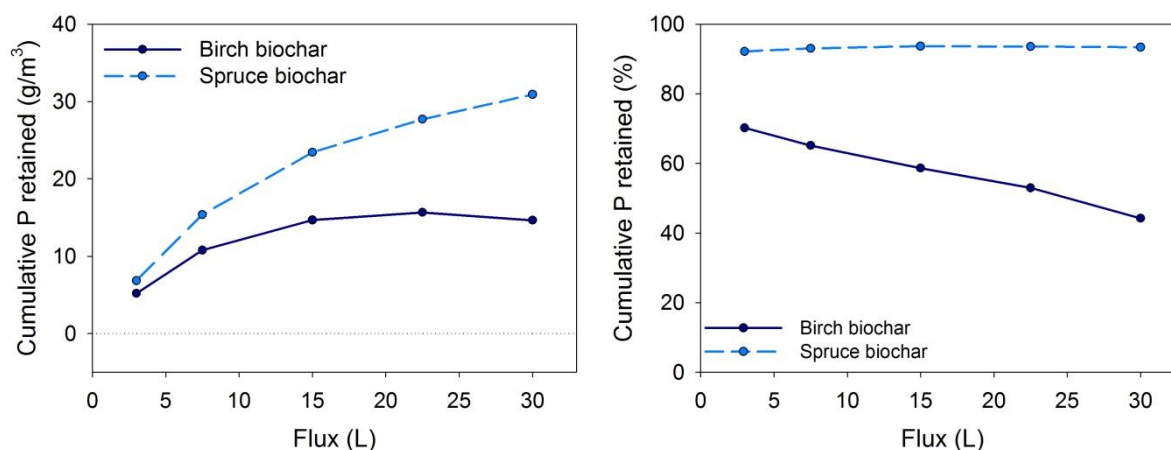


Figure 67. Cumulative phosphorus (P) retention by biochar filter materials in column experiment using 10X concentrated synthetic stormwater, expressed in g/m<sup>3</sup> (left) and as per cent of total (right).

## 6. Discussion

The most important parameter affecting the behavior of metals and phosphorus in a filter system is the pH, as pH affects both ion-solution and mineral surface chemistry. Metal sorption to the solid phase is typically low at acid pH and increases as solution pH approaches neutrality (pH 7.0). In the absence of ligands capable of forming soluble complexes with metals (i.e.  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ , organic acids), the metals will be almost entirely removed from solution at high pH through adsorption to the solid phase<sup>34</sup>.

Between 80 and 99% of the copper, lead and zinc in stormwater influent was removed by the filter materials tested (Table 7). With the exception of the birch biochar, there was no indication of decreasing metal or phosphorus removal by any of the filter materials tested after the addition of 33 liters of 1X concentrated synthetic stormwater to each column (0.002 m<sup>3</sup> reactive material per column). This quantity of stormwater influent was representative of ca. 17 370 liters of stormwater runoff per cubic meter of filter material. Results suggest that all materials examined could effectively attenuate copper, lead and zinc in stormwater runoff in the near- to mid-term (e.g.  $\leq 3$  years depending on dimensioning of the stormwater filtration system). All materials except the birch biochar could potentially be expected to remove phosphorus from stormwater runoff in the near- to mid-term.

Phosphorus was enriched in effluent from the birch biochar column relative to synthetic stormwater influent, indicating phosphorus leaching from the birch biochar solid material. The observed cumulative phosphorus enrichment in the first 33 liters of column effluent was equivalent to 5.72 g phosphorus release per cubic meter of birch biochar filter material, or a 0.33 mg/L increase in phosphorus concentration assuming passage of 17 370 liters of water through one cubic meter of filter material.

The concentration of metals and phosphorus in synthetic stormwater was subsequently increased by twenty-fold (20X) following passage of 33 liters of 1X synthetic stormwater through each column. An additional 7.5 liters of 20X concentrated synthetic stormwater were added to each column in an attempt to stimulate breakthrough of metals or phosphorus. The increase in stormwater concentration from 1X to 20X did not result in pollutant breakthrough in any of the experimental columns. In contrast, the increase in solution phosphorus

<sup>34</sup> Bradl, H.B: 2004. *Journal of Colloid and Interface Science* 277:1-18.

concentration stimulated phosphorus retention by the birch biochar. Phosphorus leaching from birch biochar was not observed following the increase in influent stormwater concentration to 20X the initial concentration, and the increased phosphorus concentration in synthetic stormwater influent resulted in net removal of phosphorus from solution by the birch biochar.

The results for phosphorus retention by birch biochar highlight the complex nature of surface sorption phenomena. Additional testing is required to fully evaluate the lability of phosphorus within the birch biochar solid matrix, including quantitation of phosphorus within the birch biochar, and measurement of phosphorus sorption and release across a range of solution concentrations and at different solution pH values (i.e. concentration and pH isotherms). The present results indicate potential for increased stormwater runoff phosphorus concentration following passage through a birch biochar filter, for example from 0.5 to 0.83 mg/L. In practice, the duration and extent of phosphorus release from birch biochar will be dependent upon multiple environmental factors as well as stormwater filter design.



Table 7. Pollutant removal from stormwater by each filter material following 33 liters of 1X concentrated synthetic stormwater flow through each respective material in laboratory column trials. Negative values highlighted in red indicate net release of the respective ion.

	SO <sub>4</sub> <sup>2-</sup>			Cl <sup>-</sup>			Cu <sup>2+</sup>			Pb <sup>2+</sup>			Zn <sup>2+</sup>			PO <sub>4</sub> <sup>3-</sup> / P <sup>5+</sup>		
	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	% <sup>a</sup>
<b>KaM 0-5</b>	-22.6	-28.8	-2.1	83.6	107	5.6	6.2	8.0	99.0	11.1	14.1	99.3	28.2	36.0	98.7	5.8	7.4	≥89.5
<b>SSr 0-16</b>	-8.2	-10.7	-0.8	56.2	73.0	3.8	6.2	8.0	99.6	11.0	14.2	99.9	28.0	36.4	99.7	5.7	7.4	≥89.5
<b>Leca 0-3 crushed</b>	-50.0	-13.0	-1.0	273	71.1	3.7	30.4	7.9	98.5	54.0	14.0	98.7	137	35.7	97.8	28.3	7.4	≥89.5
<b>Leca 2-4 round</b>	-97.3	-28.8	-2.1	226	67.1	3.5	26.8	8.0	99.0	47.7	14.1	99.3	121	35.9	98.5	24.9	7.4	≥89.5
<b>Leca 3-8 crushed</b>	-47.9	-11.8	-0.9	463	115	6.0	27.8	6.9	85.7	48.7	12.1	84.6	117	29.1	79.6	25.5	6.3	76.5
<b>Filtralite P 0.5–4 mm</b>	-38.1	-14.2	-1.1	227	84.9	4.4	21.4	8.0	99.0	38.0	14.2	99.5	96.8	36.1	99.0	19.8	7.4	≥89.5
<b>Peat</b>	44.7	9.5	0.7	372	79.0	4.1	34.9	7.4	92.1	62.2	13.2	92.6	155	32.8	89.9	34.1	7.2	87.7
<b>Peat + 10 wt.% limestone</b>	-26.0	-5.9	-0.4	372	84.9	4.4	34.7	7.9	98.4	62.4	14.2	99.9	158	36.0	98.7	32.4	7.4	≥89.5
<b>Birch biochar</b>	-70.9	-31.6	-2.3	341	152	8.0	14.7	6.6	81.7	25.4	11.3	79.5	59.8	26.6	72.9	-12.9	-5.7	-69.4
<b>Spruce biochar</b>	12.7	2.0	0.1	1857	289	15.1	49.6	7.7	96.2	87.9	13.7	96.2	219	34.2	93.7	46.6	7.3	88.0

<sup>a</sup> Where reported concentrations were less than the analytical limit of detection, a concentration equal to the limit of detection (50 µg/L) was assumed for calculation purposes. Thus, the maximum phosphorus attenuation was 89.5% and the proportion of phosphorus removed by filter materials where phosphorus concentration in effluent was less than the limit of detection was ≥89.5%.

The second column experiment using 10X concentrated stormwater was conducted to better understand the possible limitations of the materials tested with respect to treatment of particularly polluted runoff, such as surface runoff from a contaminated site. Results of column trials using 10X concentrated stormwater were similar to those obtained using 1X concentrated stormwater. Highly efficient copper, lead and zinc removal from solution by all filter materials was observed, as evidenced by the high proportion of influent metals retained within column filter materials (Table 8). Measured removal of both copper and lead from solution by the filter materials tested ranged from ca. 90–99%. Zinc attenuation was similarly high, ca. 90–96%, with the exception of the birch biochar. The birch biochar removed approximately 78% of influent zinc from the synthetic stormwater solution.

With the exception of the birch biochar, there was no indication of decreasing metal or phosphorus removal by any of the filter materials tested after the addition of 30 liters of 10X concentrated synthetic stormwater to each column (0.002 m<sup>3</sup> reactive material per column). This quantity and concentration of stormwater influent was representative of ca. 157 840 liters of 'normal' 1X concentration stormwater runoff per cubic meter of filter material. Results suggest that all materials examined could effectively attenuate copper, lead and zinc in stormwater runoff in the mid- to longer term (e.g. 5–10 years or more depending on dimensioning of the stormwater filtration system). Similarly, all materials except the birch biochar could potentially be expected to remove phosphorus from stormwater runoff in the mid- to longer term.

Results of the second column experiment using 10X concentrated synthetic stormwater indicate some potential for decreased stormwater runoff phosphorus concentration following passage through a birch biochar filter, for example from 4.0 to 3.0 mg/L; however, birch biochar showed a decline in cumulative phosphorus retention, or net release of phosphorus, between 22.5 and 30 liters of effluent flux from the column containing birch biochar (Figure 67).

Table 8. Pollutant removal from stormwater by each filter material following 30 liters of 10X concentrated synthetic stormwater flow through each respective filter material in laboratory column trials.

	Cu <sup>2+</sup>			Pb <sup>2+</sup>			Zn <sup>2+</sup>			PO <sub>4</sub> <sup>3-</sup> / P <sup>5+</sup>		
	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	%	mg/kg	g/m <sup>3</sup>	% <sup>a</sup>
<b>KaM 0–5</b>	22.9	31.0	99.1	35.4	48.1	99.4	171	232	95.2	23.4	31.7	95.9
<b>SSr 0–16</b>	23.6	31.0	99.0	36.7	48.1	99.6	178	234	96.0	24.5	32.2	97.3
<b>Leca 0–3 crushed</b>	102	29.7	95.0	159	46.4	96.0	754	220	90.5	104	30.2	91.3
<b>Leca 2–4 round</b>	109	30.3	96.9	170	47.2	97.7	786	219	89.9	111	30.8	93.0
<b>Filtralite P 0.5–4 mm</b>	86.4	30.4	97.3	135	47.4	98.1	647	228	93.7	89.0	31.4	94.8
<b>Peat</b>	123	27.9	89.0	198	44.9	92.9	935	212	92.9	126	28.4	85.8
<b>Peat + 10 wt.% limestone</b>	127	29.9	95.5	204	48.1	99.5	970	229	93.9	132	31.1	93.9
<b>Birch biochar</b>	67.1	27.6	88.1	107	44.0	91.0	463	190	78.2	35.6	14.6	44.2
<b>Spruce biochar</b>	237	30.5	97.3	370	47.5	98.2	1734	223	91.4	241	30.9	93.4

Analyses of 10X concentrated synthetic stormwater influent showed a notable decrease in metal and phosphorus concentration with time, and a concomitant increase in pH (Figure 68). Calculated Pearson product-moment correlation coefficients showed a strong inverse relationship between the synthetic stormwater pH and the concentrations of phosphorus ( $r = -0.88$ ), copper ( $r = -0.82$ ), lead ( $r = -0.83$ ) and zinc ( $r = -0.91$ ) in solution.

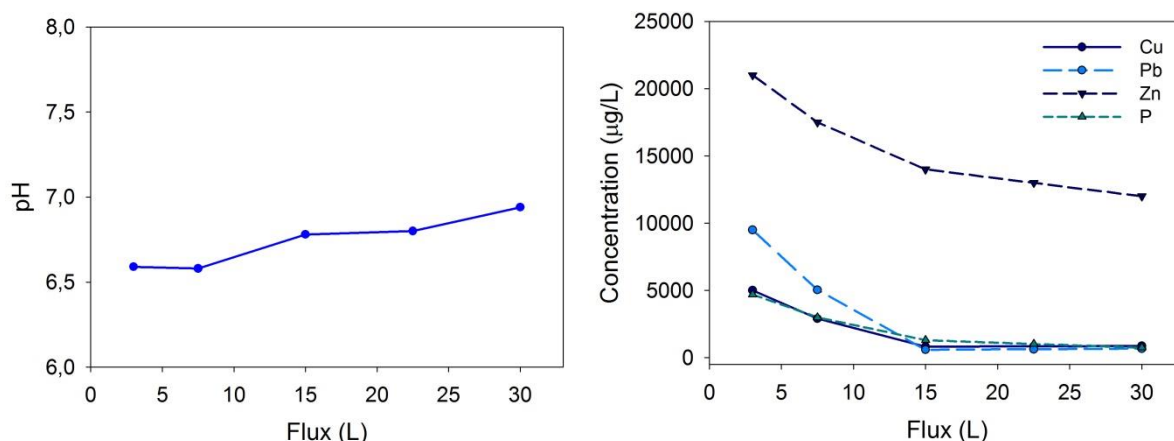


Figure 68. The pH (left) and analyte concentration (right) of the 10X concentrated synthetic stormwater used in the second set of column experiments, shown as a function of time expressed in cumulative addition to columns (flux, in L).

## 7. Conclusions

Protection or restoration of both freshwater and marine receiving waters to meet water quality objectives is increasingly accomplished using decentralized engineered water management structures to trap, infiltrate and/or harvest stormwater. Numerous studies have shown that vegetated stormwater filters can attenuate biochemical oxygen demand (BOD), suspended solids, nutrients, pesticides and polycyclic aromatic hydrocarbons (PAHs) in stormwater runoff<sup>35,36,37</sup>. Examples of stormwater management systems include: retention basins to store rather than convey stormwater; engineered wetlands to attenuate contaminants in stormwater prior to discharge to natural ecosystems; pervious pavements, buffer strips and biofiltration swales to remove suspended solids and encourage groundwater recharge; rain gardens, green roofs and other bio-retention systems which use vegetation to remove particulate and soluble contaminants, take up nutrients, and promote evapotranspiration; and, rain tanks for capture and use of stormwater for localized irrigation or other non-potable applications. In recent years, Finland has been active in reintroducing green roofs<sup>38</sup> as well as pervious pavements<sup>39</sup>, though these solutions focus on filtration for stormwater quantity rather than water quality.

Results of the present study show that engineered passive stormwater infiltration systems containing reactive geomedia can improve stormwater quality prior to water infiltration, uptake by collection systems or discharge to receiving waterbodies. This will in turn reduce pollutant loads to aquatic environments, thereby reducing pressure on over-exploited water resources. In addition to returning clean freshwater to ecosystems, stormwater purification

<sup>35</sup> Bhatia, M., D. Goyal. 2014. *Environmental Progress & Sustainable Energy* 33(1):9-27.

<sup>36</sup> Ladislav, S., C. G  rente, F. Chazarenc, J. Brisson, Y. Andr  s. 2015. *Ecological Engineering* 80:85-91.

<sup>37</sup> Zhang, K., A. Randelovic, D. Page, D.T. McCarthy, A. Deletic. 2014. *Ecological Engineering* 67:1-10.

<sup>38</sup> Fifth Dimension Project, <http://www.luomus.fi/en/fifth-dimension-green-roofs-urban-areas>

<sup>39</sup> CLASS – Climate Adaptive Surfaces, Tekes project # 1987/31/2012 (years 2012-14).

also facilitates its use as an alternative to potable water supplies and contributes long-term water resource sustainability.

All of the materials examined herein showed strong potential for use filtration materials to attenuate metals and/or phosphorus from stormwater runoff. Although it was not possible to conclusively estimate individual contaminant capacities for each of the respective filter materials, results indicate a likely effective lifespan in the range of up to ca. 10 years in the absence of physical clogging or similar malfunctions, and depending upon the design and scale of the filtration structure implemented.

The lack of substantial differentiation between pollutant removal by nominally unreactive aggregate filter materials and those known to possess high cation exchange capacity or specific surface reactivity towards phosphate ions suggests that the mechanism by which metals and phosphorus were retained by filter materials may have been primarily physical or a combination of physical and chemical mechanisms. Solution pH significantly influenced metal and phosphorus solubility, with decreased concentrations of metals and phosphorus in influent synthetic stormwater strongly correlated with increases in solution pH. The formation of flocs or metal precipitates as solution pH increased may provide a partial explanation for physico-chemical mechanisms of metal and phosphorus retention by the filter materials examined herein. Additional testing under controlled pH conditions, i.e. with maintenance of influent synthetic stormwater at pH of approximately 6.5, is necessary to differentiate material surface chemical interactions from physical entrapment of elements flocculated within or precipitated from solution during passage through filter materials.

Laboratory column experiments and a meso-scale upscaling experiment are presently underway using various combinations of filter materials in layers to investigate potential synergistic or antagonistic effects on metal (copper, lead and zinc) and phosphorus removal from synthetic stormwater. The pH of influent stormwater will be maintained at pH 6.2-6.5 to minimize flocculation and/or precipitation of metals and phosphorus in the stormwater solution. Geochemical modelling will be used to identify potential geochemical mechanisms of metal and phosphorus retention by the layered filter materials. These experiments are ongoing and will be reported separately in August 2017.

## Appendix I. Synthetic stormwater in StormFilter laboratory tests

Literature regarding the Finnish stormwater runoff composition was reviewed (Sillanpää 2007, Vaahtera 2013, Inha et al. 2013, Airola et al. 2014, Sänkiäho & Sillanpää 2012). Focus was on the maximum observed concentrations for pollutants in order to have an understanding of a worst case scenario. The literature reviewed contained data from Helsinki, Tampere, Vaasa, Kajaani, Oulu, Hyvinkää and Lahti. The maximum observed concentrations for the most commonly reported constituents are presented in Table A1.

*Table A1. Maximum observed concentrations for the most commonly reported constituents of stormwater from Helsinki, Tampere, Vaasa, Kajaani, Oulu, Hyvinkää and Lahti.*

Stormwater Constituent	Concentration (µg/l)
<b>Cu</b>	900
<b>Pb</b>	1 500
<b>Zn</b>	5 000
<b>Cr</b>	860
<b>Cd</b>	2,8
<b>Ni</b>	124
<b>Total nitrogen</b>	1 364
<b>Total phosphorus</b>	161
<b>Cl</b>	3 600 000
<b>SO<sub>4</sub></b>	87 000

The information in Table A1 was sent to StormFilter project partners for comments. Suggestions were made to decrease some concentrations in order to make the scenario more realistic. International literature was also reviewed (Al-Anbari et al. 2008, Göbel et al. 2007, Reddy et al. 2014, Westerlund & Viklander 2006, Lind et al. 2001) to obtain a broader perspective on typical stormwater constituent concentrations. An-Albari et al. reported maximum Cu, Pb and Zn loads of 469, 653 and 1600 µg/l, respectively, during a first flush event from an impervious multi storey car park. Göbel et al. made a comprehensive review of stormwater runoff compositions consisting of more than 300 references. They reported maximum concentrations of 925, 2 000 and 340 µg/l for Pb, Zn and total P, respectively, from trafficked areas with high density. Average concentrations from motorways for chloride and sulphate were 159 000 and 39 000 µg/l, respectively.

Based on suggestions from project partners and additional review of international literature, adjustments were made to the proposed water composition. The principal of high concentrations was retained in order to simulate a worst case scenario (e.g. first flush following prolonged dry period) in the laboratory tests and to accelerate simulated ageing in order to obtain estimates of material lifetime (capacity) within a reasonable timeframe. Some constituents were excluded from the final water composition due to limited resources available and a large amount of samples to be tested for the chemical composition. Dissolved organic carbon (DOC) was added as a constituent because DOC is a ubiquitous component of surface waters and affects metal binding mechanisms and surface interactions via sorption and ligand exchange processes. The final synthetic stormwater composition is presented in Table A2.



Table A2. StormFilter project synthetic stormwater composition for use in laboratory testing.

Pollutant	Concentration (µg/l)
<b>Cu</b>	500
<b>Pb</b>	1 000
<b>Zn</b>	2 000
<b>Total phosphorus</b>	500
<b>Cl</b>	100 000
<b>SO<sub>4</sub></b>	80 000
<b>Humic acid (DOC)</b>	10 000

The synthetic stormwater was produced using tap water. Water purification plants in Espoo area use chloramine to control microbiological contaminants in the distributed water. However, the quantity (0.03–0.5 mg/l) of chloramine used is low and reduced in concentration as water passes through the distribution system to yield a negligible concentration of chloramine in water obtained from a tap in the Espoo area. Chloramine traces in the tap water are not regarded as a concern, particularly as the added humic acid in the synthetic stormwater mixture will neutralize any trace chloramines potentially present in the tap water. Due to the large volume of water required for laboratory tests (hundreds of litres), tap water is the most cost-effective starting material for synthetic stormwater generation.

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## Appendix II. Results of Filter Material Batch Sorption Experiments

Table A3 shows the raw data obtained from batch sorption experiments using 135 g of a single “test” material in 1,35 L synthetic stormwater. See Table 3 for details of initial stormwater composition. Data shown in Figure 2–Figure 7 represent means of triplicate subsamples.

*Table A3. Composition of synthetic stormwater following 24 h end-over-end mixing with individual test materials.*

Material	Solid material (g)	Solution (g)	L/S ratio	pH	Stormwater composition (µg/L)					
					SO <sub>4</sub>	Cl	Cu	Pb	Zn	P
Control		1350,06		7,16	71910	91000	250	290	1800	430
		1350,01		7,13	71910	89000	250	290	1700	450
		1350		7,30	71910	77000	230	230	1700	420
		1350,02		6,76	77000	110000	130	140	1500	320
Plastic, used in column tests	10 cm <sup>2</sup> (0,99g)	1350,03		7,26	71910	108000	220	230	1700	420
	10 cm <sup>2</sup> (1,02g)	1350,03		7,28	71910	95000	220	230	1700	410
	10 cm <sup>2</sup> (0,99g)	1350,04		7,41	71910	90000	210	180	1700	390
SSr 0-16	135,04	1350,03	10,0	7,29	71910	95000	160	260	490	270
	135,05	1350,04	10,0	7,22	71910	96000	140	220	490	250
	135,01	1350	10,0	7,11	71910	92000	170	220	560	300
KaM 0-5	135,11	1350,13	10,0	7,46	71910	90000	200	340	880	460
	135,10	1350,11	10,0	7,43	71910	88000	170	260	840	440
	135,04	1350,04	10,0	7,76	71910	106000	150	210	770	370
Leca 0-3mm crushed	135,09	1349,98	10,0	9,76	77903	103000	51	49	110	200
	135,04	1350,04	10,0	9,65	74906	102000	50	45	100	240
	135,01	1350	10,0	9,65	74906	90000	42	25	110	220
Leca 2-4mm round	135,10	1350,34	10,0	8,98	74906	88000	160	140	450	340
	135,00	1350	10,0	8,82	74906	107000	130	120	410	310
	135,02	1350,02	10,0	9,25	74906	86000	140	120	430	300
Leca 3-8mm crushed	135,05	1350	10,0	9,12	74906	87000	140	150	530	340
	135,04	1350,01	10,0	9,15	74906	90000	120	130	490	330
	135,00	1350	10,0	9,32	74906	92000	140	99	470	300
Filtralite P 0.5-4mm	135,17	1351,63	10,0	9,82	77903	86000	130	110	500	220
	135,01	1350,03	10,0	9,75	77903	79000	120	110	520	220
	135,01	1350,03	10,0	9,74	80899	83000	71	66	280	130
Peat	135,10	1350,26	10,0	4,25	74906	95000	28	4,6	170	61
	135,02	1350,04	10,0	4,14	74906	109000	22	4,7	160	<50
	135,01	1350,06	10,0	4,35	83000	110000	26	4,6	160	<50
Peat (3-16mm) + limestone (10%)	134,98	1350,04	10,0	6,47	85000	110000	24	3,2	64	<50
	135,05	1350,03	10,0	6,49	85000	110000	10	2,2	49	<50
	135,00	1350,00	10,0	6,52	84000	110000	21	2,8	51	<50
Biochar, untreated	135,01	1350,02	10,0	7,45	74906	105000	8,4	3,1	260	180
	135,01	1350,02	10,0	7,71	74906	97000	9,4	4,1	260	190
	135,00	1350,01	10,0	8,25	74906	114000	30	15	260	210
Biochar, sieved (<5,6 mm)	135,03	1350,02	10,0	8,11	74906	98000	11	4,3	120	130
	135,00	1350,01	10,0	8,11	74906	80000	9,7	4,8	130	140
	135,00	1350,01	10,0	8,05	74906	107000	12	6,8	150	180
Biochar, birch, koivu	135,02	1350,06	10,0	8,68	190000	110000	5,2	0,5	7	1300
	135,06	1350,07	10,0	8,68	180000	110000	5,3	0,4	7	1300
	135,05	1350,05	10,0	8,65	220000	110000	7,1	0,9	11	1400
Biochar, spruce, kuusi	135,00	1350,39	10,0	8,23	78000	99000	3,4	2,9	48	140
	135,01	1350,07	10,0	8,24	76000	99000	3,4	2,4	38	160
	135,01	1350,05	10,0	8,20	77000	99000	3	2,9	46	140

## Appendix III. Results: First Column Experiment

Table A4 shows the raw data obtained from column experiments using a single “test” material (between layers of aggregate, see Figure 8) within each column. Initial stormwater composition was the same as used in batch material testing (1X Nominal Concentration, see Table 5). Column effluents were analyzed using inductively-coupled plasma spectrophotometry – atomic emission spectroscopy (ICP-AES). Values shown in red text indicate a net increase in measured effluent concentration relative to influent.

Table A4. Composition of influent synthetic stormwater and effluents from laboratory columns containing individual test materials.

Material	Cumulative flux (L)	pH	Concentration (µg/l)					
			SO <sub>4</sub>	Cl	P	Cu	Pb	Zn
Synthetic stormwater (influent)	1.5	7,84	77500	110000	475	462,5	820	2100
	6	7,57	77500	110000	475	462,5	820	2100
	15	7,22	77500	110000	475	462,5	820	2100
	24	7,37	77500	110000	475	462,5	820	2100
	33	7,34	77500	110000	475	462,5	820	2100
	36	6,25			9200	9000	17000	42000
	40,5	6,32			9200	9000	17000	42000
KaM 0–5 mm	1.5	7,20	51000	56000	<50	14	23	80
	6	7,74	82000	110000	<50	4,0	4,4	22
	15	7,32	84000	110000	<50	3,2	2,5	14
	24	7,73	82000	110000	<50	3,3	3,3	21
	33	7,44	83000	110000	<50	4,1	4,8	26
	36	7,76			<50	1,9	0,3	330
	40,5	7,30			<50	2,6	0,3	420
Leca round 2–4 mm	1.5	7,51	51000	52000	<50	11	17	66
	6	7,68	82000	110000	<50	4,3	5,3	24
	15	7,41	84000	120000	<50	5,1	6,2	38
	24	7,76	82000	110000	<50	3,6	3,9	25
	33	7,48	83000	110000	<50	2,9	2,3	14
	36	7,78			<50	1,7	0,1	180
	40,5	7,25			<50	2,4	0,1	180
SSr 0–16 mm	1.5	7,56	46000	49000	<50	2,5	0,5	5
	6	7,71	81000	110000	<50	1,9	0,5	8
	15	7,48	84000	120000	<50	1,8	0,6	7
	24	7,71	81000	110000	<50	1,7	0,2	5
	33	7,55	83000	110000	<50	1,9	0,9	6
	36	7,65			<50	1,3	0,1	79
	40,5	7,22			<50	1,5	0,1	120
Leca crushed 0–3 mm	1.5	7,49	49000	50000	<50	12	18	54
	6	7,86	80000	110000	<50	8,6	14	67
	15	7,52	84000	120000	<50	5,0	5,9	27
	24	7,78	81000	110000	<50	7,0	11	53
	33	7,56	83000	110000	<50	5,5	7,8	35
	36	7,41			290	40	9,5	2200
	40,5	7,08						
Leca crushed 3–8 mm	1.5	7,44	49000	52000	140	100	160	520
	6	7,63	81000	110000	120	79	130	490
	15	7,44	83000	110000	110	66	140	440
	24	7,67	81000	110000	96	50	110	350
	33	7,46	83000	110000	110	50	100	390
	36	7,40			500	220	290	3300
	40,5	7,12			600	320	500	3900
Peat	1.5	7,07	46000	46000	68	47	65	230
	6	6,73	80000	110000	<50	29	34	120
	15	6,53	82000	120000	73	51	100	330
	24	6,75	80000	110000	<50	27	36	150

Material	Cumulative flux (L)	pH	Concentration (µg/l)					
			SO <sub>4</sub>	Cl	P	Cu	Pb	Zn
	33	6,51	82000	110000	<50	30	65	230
	36	6,41			170	48	23	1200
	40,5	6,43			170	49	18	1500
Peat + 10% limestone	1.5	6,79	46000	43000	<50	9,6	0,7	15
	6	6,59	81000	110000	<50	9,3	1,4	30
	15	6,19	83000	120000	<50	6,9	0,8	26
	24	6,63	81000	110000	<50	6,4	1,1	26
	33	6,56	83000	110000	<50	7,3	1,9	32
	36	6,56			98	33	1,8	750
	40,5	7,17			120	33	1,5	1100
Biochar koivu/birch	1.5	8,07	53000	51000	300	100	160	680
	6	8,06	83000	100000	760 <sup>T</sup>	71	120	500
	15	7,88	83000	110000	870	90	200	600
	24	7,94	82000	110000	960	93	190	580
	33	8,01	83000	110000	850	65	140	490
	36	8,02			1800	480	680	6100
	40,5	7,90			1500	330	510	4400
Biochar kuusi/spruce	1.5	8,00	42000	36000	110	82	140	440
	6	8,04	81000	83000	<50	12	25	120
	15	7,90	83000	100000	<50	12	21	120
	24	7,93	81000	110000	<50	7,2	13	68
	33	8,03	83000	110000	<50	5,3	9,2	47
	36	7,89			94	3,0	0,5	820
	40,5	7,72			120	4,5	0,4	1100
Filtralite crushed 0.5–4 mm	1.5	8,02	43000	43000	<50	5,2	6,8	24
	6	7,88	81000	110000	<50	2,3	1,7	12
	15	7,81	84000	120000	<50	3,0	3,9	27
	24	7,83	83000	110000	<50	2,8	3,9	17
	33	7,87	83000	110000	<50	3,7	5,7	24
	36	7,67			53	1,6	0,4	470
	40,5	7,69			59	1,2	0,1	520

## Appendix IV. Results: Second Column Experiment Using 10X Concentrated Stormwater

Table A5 shows raw data obtained from column experiments using a single “test” material (between layers of aggregate, see Figure 8) within each column. Influent stormwater composition was concentrated ten-fold relative to that used in batch material testing (10X Nominal Concentration, see Table 6). Column effluents were analyzed using inductively-coupled plasma spectrophotometry – atomic emission spectroscopy (ICP-AES).

Table A5. Composition of influent synthetic stormwater and effluents from laboratory columns containing individual test materials.

Material	Cumulative flux (L)	pH	Concentration (µg/l)			
			P	Cu	Pb	Zn
Synthetic stormwater (influent)	3,0	6,59	4700	5000	9500	21000
	7,5	6,58	3000	2910	5045	17500
	15,0	6,78	1300	820	590	14000
	22,5	6,80	1025	845	635	13000
	30,0	6,94	750	870	680	12000
KaM 0–5 mm	3,0	7,38	190	64	65	1600
	7,5	7,31	110	15	18	1200
	15,0	7,44	50	6,1	4,8	360
	22,5	7,32	50	9	6	400
	30,0	7,75	50	6,2	5,1	270
Leca round 2–4 mm	3,0	7,38	270	140	170	1900
	7,5	7,23	240	65	89	2100
	15,0	7,31	85	28	22	1300
	22,5	7,22	88	46	48	1400
	30,0	7,55	60	47	41	1100
SSr 0–16 mm	3,0	7,54	77	28	19	490
	7,5	7,49	51	5	2,7	500
	15,0	7,37	51	13	8,3	640
	22,5	7,29	53	25	17	750
	30,0	7,55	50	28	24	720
Leca crushed 0–3 mm	3,0	7,47	340	210	290	2000
	7,5	7,30	230	88	140	1900
	15,0	7,28	160	93	120	1500
	22,5	7,40	96	60	25	970
	30,0	7,61	110	54	48	970
Leca crushed 3–8 mm	3,0	7,07	1700	1300	1800	9200
	7,5	7,01	1700	1400	2000	9400
	15,0	6,95	1700	1800	2800	9900
	22,5	6,90	1600	2200	3300	9700
	30,0	7,17	1500	2200	3400	9700
Peat	3,0	7,29	600	390	510	3500
	7,5	6,75	530	340	380	3300
	15,0	6,50	150	100	43	1200
	22,5	6,48	110	110	61	1000
	30,0	6,66	170	230	220	1600
Peat + 10% limestone	3,0	7,45	130	38	34	940
	7,5	6,86	140	70	22	880
	15,0	6,50	150	94	9,3	1100
	22,5	6,49	120	130	5,3	950
	30,0	6,68	80	100	4	710
Biochar koivu/birch	3,0	7,61	1400	840	1000	8000
	7,5	7,87	1600	190	240	4300
	15,0	7,98	720	110	130	2500

Material	Cumulative flux (L)	pH	Concentration (µg/l)			
			P	Cu	Pb	Zn
	22,5	7,99	1100	59	52	1300
	30,0	8,12	1200	62	63	1200
Biochar kuusi/spruce	3,0	7,72	370	150	170	2500
	7,5	7,69	110	22	16	960
	15,0	7,63	110	36	33	1300
	22,5	7,64	55	21	14	920
	30,0	7,74	86	63	73	1100
Filtralite crushed 0.5–4 mm	3,0	8,02	260	140	180	1400
	7,5	7,88	93	42	41	710
	15,0	7,81	70	25	33	1300
	22,5	7,83	71	35	31	720
	30,0	7,69	70	43	31	660